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Suggestions to Authors of the Reports of the United States Geological Survey, 5th ed. Washington, D. C., 1958 (Government Printing Office, $1.75).

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JUNE 1960

MOLECULAR DIFFUSION RATES IN SUPERCRITICAL WATER VAPOR ESTIMATED FROM VISCOSITY DATA

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ABSTRACT. According to the Stokes-Einstein equation the diffusivity of a particle in a gas is a function of the radius of the particle, the absolute temperature, and the viscosity of the gas. Recent theoretical and experimental results are used to extrapolate values for the viscosity of supercritical water vapor up to 800°C. and 2,500 kg cm^{-2} pressure. The function Dr_s is evaluated in this range, where D is the diffusivity and r_s the radius of a molecular particle in solution in supercritical water vapor. It is shown that molecular components of rocks should have diffusion rates on the order of 10^{-3} to 10^{-4} cm^2sec^{-1} over a wide range of geologic pressures and temperatures. As an example these results are applied to an evaluation of the diffusivity of silica in supercritical water vapor, and it is shown that the mass transport of silica by diffusion is potentially a relatively rapid geologic process where supercritical water vapor exists at high pressures in the intergranualr spaces in rocks, even where the effective directional porosity of the rock is several orders of magnitude less than one. Values for viscosity of water, Dr_s, solubility in water of SiO_2 in gm cm^{-3}, mass transport of SiO_2, and mean square displacement of SiO_2 in supercritical water vapor are given graphically for various temperatures up to 800°C. and pressures up to 2,500 kg cm^{-2}.

The properties of water in the range of several hundred to a thousand degrees centigrade and up to several thousand atmospheres of pressure are of great interest, especially in geology. Thanks largely to the work of Kennedy (1950; Holser and Kennedy, 1958, 1959) considerable equilibrium PvT data are now available in this range. However, the so-called non-equilibrium or transport properties have as yet received little systematic attention from geologists. These properties, viscosity, thermal conductivity, diffusivity, etc., are the properties which determine the capacity of water to serve as a vehicle for the transfer of matter and energy. In this paper an attempt is made to estimate the capacity of supercritical water to serve as a medium for the diffusion of molecular particles.

Available experimental data on the non-equilibrium properties of water do not extend very far into the range of geologic pressures and temperatures. To get some idea of how supercritical water behaves in this range it is necessary to make empirical or theoretical extrapolations. Unfortunately no common gas is more intractable to theoretical extrapolation than water vapor because of the extreme polarity of the water molecule.

Diffusivity of a particle in a fluid medium is given by the well-known Stokes-Einstein equation:

$$(1) \qquad D = \frac{RT}{6\pi N \eta r_s}$$

Where D is diffusivity, R is the gas constant, T the absolute temperature, N Avogadro's number, r_s the radius of the particle, and η the viscosity of the fluid

medium. It is assumed that the concentration of the diffusing particle is too low to affect the properties of the fluid, that the particle is essentially spherical and large enough so that the fluid behaves as a continuous medium, and that there is no interaction between the particle and the fluid other than the transfer of momentum. Since these assumptions are not true with respect to molecular particles in a real gas, the equation is at best an approximation. It has been found, for example, in gases at high pressure that better agreement with experimental results is obtained if the numerical coefficient in the denominator is 4 instead of 6 (Prof. P. A. Lyons, Chemistry Department, Yale University, personal communication). On the other hand, the effect of non-ideality of a real gas is to some degree manifested in this equation by variation in η with T and P, so that if a good approximation can be made of η, the departure from ideality may be partly compensated.

I propose to use this equation to get an approximate notion of the rates at which molecular components of rocks and minerals might diffuse through supercritical water vapor. If the results are of even order of magnitude validity they will be highly significant for geology.

Evaluating the constant $(R/4\pi N)$ in equation (1) and transposing:

$$(2) \qquad Dr_s = \frac{T}{\eta} 1.1 \times 10^{-17} \text{erg deg}^{-1}$$

The viscosity is, of course, a specific property which varies with T and P. The problem is to extrapolate experimental values for viscosity into the range of geologic temperatures and pressures. Recently Fano, Hubbell, and Beckett (1956) derived functions for the viscosity of water at higher temperatures and pressures which allow in some measure for the non-ideality of water vapor by adjusting the Chapman-Enskog theory of dense gases (Hirschfelder, Curtiss, and Bird, 1956, p. 649) to the PvT data of Kennedy. Their calculated values for viscosity are almost all within 10 percent and generally within 5 percent of the measured values of Timroth (1940), Sigwart (1936a,b), and Jackson (1949), which extend to 600°C and several hundred atmospheres pressure.

Fano, et al. (1956, p. 11) give an empirical function for the so-called zero pressure viscosity of water vapor (which is for all practical purposes the viscosity at 1 atmosphere within the geologic range of temperature):

$$(3) \qquad \eta_T = 0.361\,T - 10.2, \text{ for } T \leqslant 800°K.$$

$$(4) \qquad \eta_T = \frac{39.37\,T^{3/2}}{33.15 - T + 0.001158\,T^2}, \text{ for } T \geqslant 800°K.$$

The values for η_T derived from these equations compare closely with values obtained by Krieger (1951) in an extrapolation of zero pressure viscosity to higher temperatures in which an effort was made to take into account the dipole interaction of the polar molecule.

To obtain the viscosity at higher pressures the following function is given:

$$(5) \qquad \eta/\eta_T = 1 + 0.175\,b\rho + 0.8651\,b^2\rho^2$$

in which η_T is $\eta_{(1\text{ atmos.})}$ at stated T, ρ is the density of water vapor at stated T and P, and b is obtained from the following:

$$(6) \qquad b = \frac{1.783}{M^{1/4}} \left(\frac{\sqrt{T}}{\eta_T} \right)^{3/2} \times 10^{-7}$$

in which M is molecular weight of water. Values for the viscosity of water vapor at various temperatures and pressures obtained from these functions are

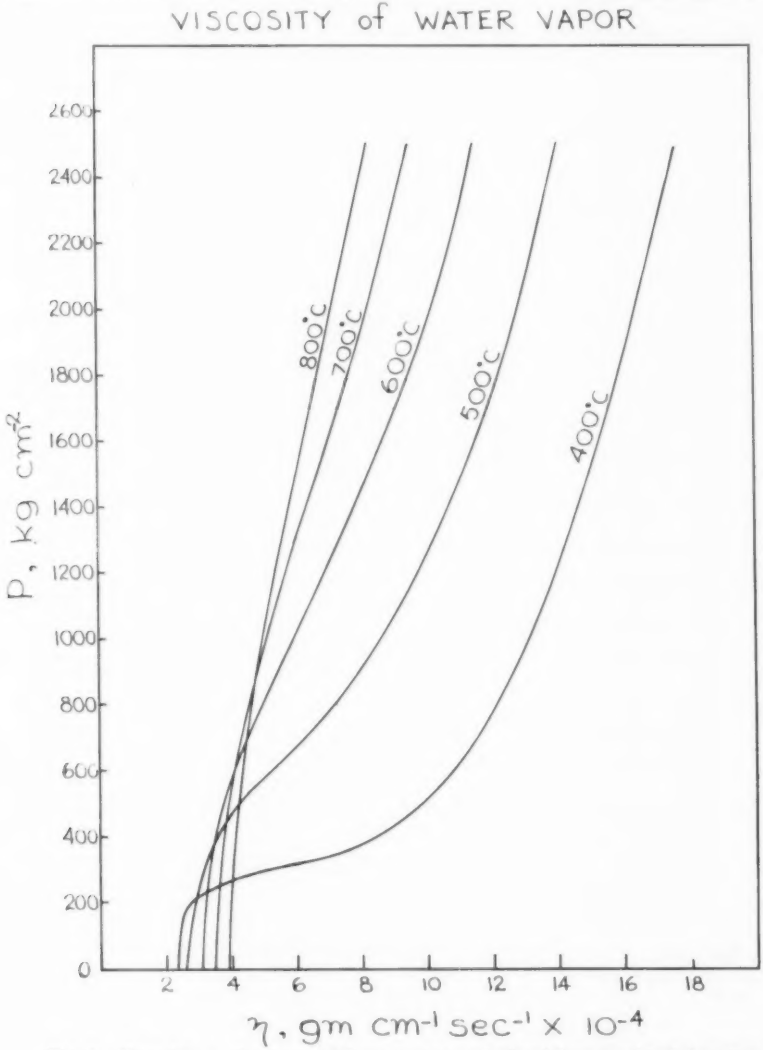

Fig. 1. Viscosity, η, of supercritical water vapor calculated from empirical functions of Fano, et al. (1956).

presented in column 4 of table 1, and are shown graphically in figure 1. Values for density used in the calculation were obtained from Kennedy's tables (Kennedy, 1950; Holser and Kennedy, 1958, 1959) and are given in column 3 of table 1.

Better than order-of-magnitude significance for these calculated viscosities seems reasonable since the values lie between the values for liquid water in equilibrium with water vapor just below critical pressure and temperature, which are on the order of 10^{-3} poise, and the values for water vapor at low pressures and temperatures, which are somewhat less than 10^{-4} poise. The viscosity of a liquid tends to decrease with increasing temperature, while the viscosity of a gas increases. It is not surprising that the viscosity of supercritical water vapor at high pressures exceeds the viscosity of very hot water just below critical temperature. The lowest experimental value obtained by Timroth for the viscosity of liquid water is 6.8×10^{-4} poise at 360°C. and 200 kg cm^{-2} pressure. This is less than the viscosity for supercritical water vapor in the upper range of pressures for which calculations have been made.

Values for the function Dr_s for supercritical water vapor obtained from equation (2) are given in column 5 of table 1, and are shown graphically in figure 2. The characteristics of this function have interesting geologic implications. Once beyond the critical region of pressure and temperature the function becomes slowly varying with respect to both T and P over a fairly wide and significant range of geologic pressures and temperatures. To the extent therefore that the diffusion of molecular particles is dependent on the viscosity and kinetic energy of the water vapor, diffusion rates should vary within less than an order of magnitude over a considerable geologic range. Moreover, it is probable that the kinds of particles, such as molecues and hydrated ions, which diffuse in water vapor have radii (r_s) ranging from a little less than one to three or four ångstroms. Consequently diffusion coefficients in supercritical water vapor should fall in the range of 10^{-3} to 10^{-4} cm^2sec^{-1} under geologic conditions ranging from high temperature hydrothermal processes to moderate and high-grade metamorphism and magmatic processes, so long as the concentration of solutes in the vapor does not become large enough to seriously modify the properties of the gas.

To illustrate the application of this function, diffusion rates are calculated for silica in water vapor. The values are given in column 6 of table 1 and shown graphically by referring to the lower scale on the abscissa of figure 2. It is assumed that silica occurs in solution in supercritical water vapor as a tetrahedrally coordinated $Si(OH)_4$ molecule (Wasserburg, 1958). It would appear reasonable to assume that $Si(OH)_4$ is structurally analogous to other hydroxy-acids of the form $A(OH)_n$ which have been investigated in which the OH^- ions cluster around each cation and adjacent clusters are linked by (OH)-(OH) bonds. These bonds range in length from 2.70 Å to 2.82 Å (Wells, 1945). The ionic radius of $(OH)^-$ is approximately the same as that of O^{2-} (Wyckoff, 1931, p. 192), and so I will take as an estimate of the radius of the free particle, $Si(OH)_4$, the observed interatomic distance in the tetrahedral ion SiO_4^{4-} as given by Pauling (1945, p. 240), which is 1.60 Å, plus

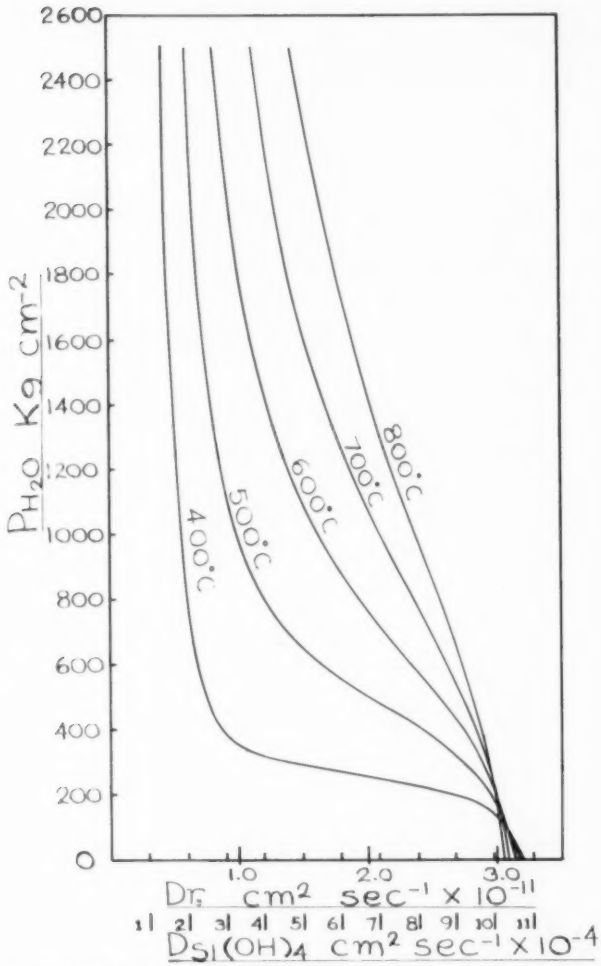

Fig. 2. Stokes-Einstein diffusion function for supercritical water vapor. Upper scale on abcissa gives values for product of diffusivity, D, and radius of solute particle, r_s. Lower scale gives values for diffusivity of hydrated silica molecule, $D_{Si(OH)_4}$.

one half the average (OH)-(OH) bond, which is 1.38 Å, giving a value for r_s of 2.98 Å

The calculated diffusion rate for silica in supercritical water vapor ranges from about 10^{-4} cm^{2}sec^{-1} to 10^{-3} cm^{2}sec^{-1}. Diffusion rates of this order are large enough to produce very large transfers of material within geologically short periods of time. By comparison the diffusivities of common salts in water

at s.t.p. are on the order of 10^{-6} to 10^{-5} cm^2sec^{-1}. The diffusion rate of glycerol at 0.1 molar concentration in water at 10°C is 4.13×10^{-6} cm^2sec^{-1} (molecular weight of glycerol, 92; $Si(OH)_4$, 96).

As a basis for estimating the geologic significance of diffusion in supercritical water vapor a system may be considered where in one region the vapor is saturated with silica at a given temperature and pressure and in another region the silica is virtually quantitatively removed by reaction to form an insoluble compound. Such a system would be approximated by the experiment described by Bowen and Tuttle (1949) where crucibles containing finely divided silica and MgO are placed side by side in a hydrothermal bomb. In a very short time forsterite crystals form in the crucible containing MgO by diffusion of silica through the vapor, but no such crystals form in the silica crucible because MgO and forsterite are virtually insoluble in supercritical water vapor. The concentration gradient in the vapor in such a system should approach the solubility of silica in the vapor.

I have converted the data given by Morey (1957) on the solubility of silica in water vapor to grams per cc, using Kennedy's tables for the specific volumes. These data are plotted in figure 3. Values taken from these curves for

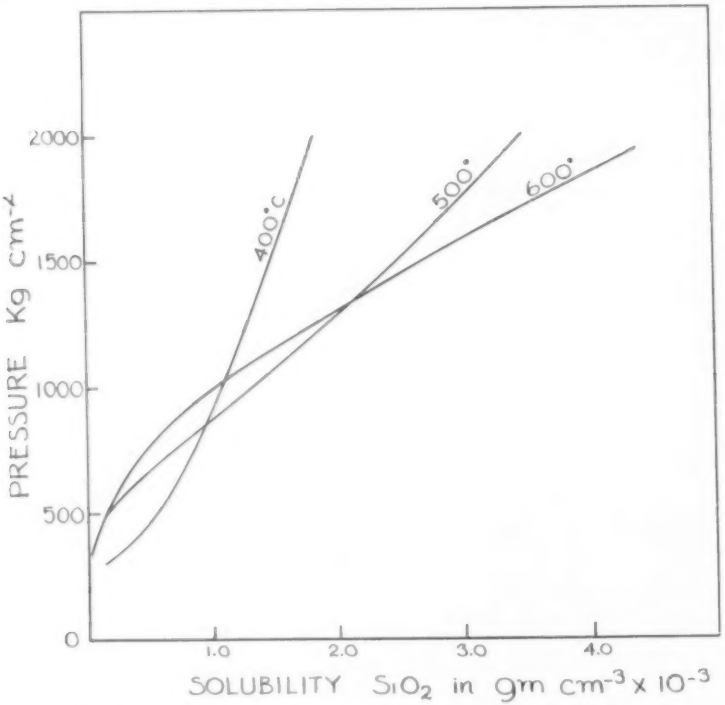

Fig. 3. Solubility of silica in supercritical water vapor in gm cm^{-3}.

the concentration of silica in saturated water vapor are given in column 7 of table 1. Morey's data on solubility covers only part of the range of P and T for which I have calculated viscosity and diffusivity, but enough to illustrate the possible magnitude of silica transport in supercritical water vapor.

Fick's equation for mass transport where diffusion is driven by a concentration gradient is:

$$(7) \qquad m = -DA \frac{(\Delta C)t}{l}$$

where m is the mass of solute diffused through a cross-section area, A, in time t, D is the diffusivity of the solute in the solution, and ΔC is the change in concentration over a distance l. Assuming the concentration falls from saturation to zero between two regions at a given T and P, the mass transport is:

$$(8) \qquad m = M' \frac{At}{h}$$

where:

$$(9) \qquad M' = DC'$$

D being the diffusivity of the solute at stated T and P, and C′ its solubility in

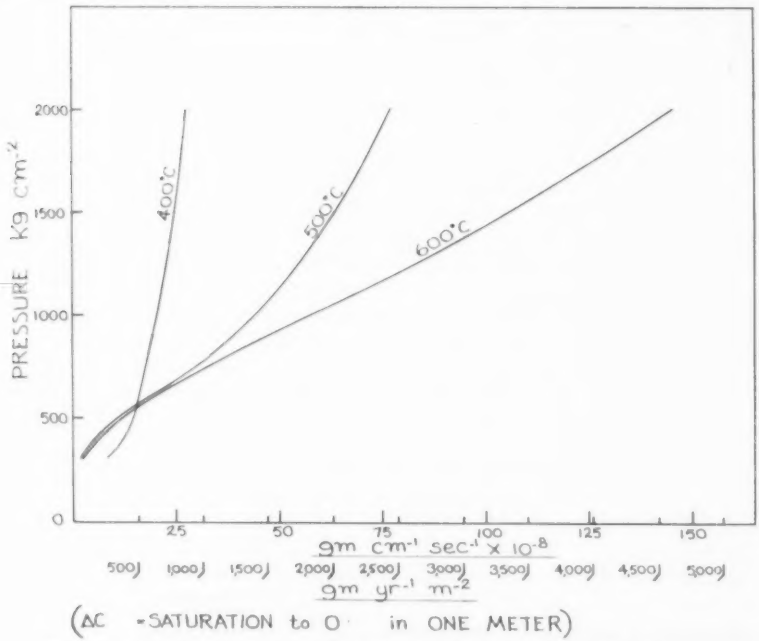

Fig. 4. Calculated mass transport of silica by diffusion in supercritical water vapor. Upper scale on abcissa gives values for a concentration gradient, ΔC, of saturation to 0 in 1 cm. Lower scale gives values for a concentration gradient of saturation to 0 in 1 m.

grams per cc at stated T and P. Values for M′ for silica in supercritical water vapor are given in column 8 of table 1 and shown graphically in figure 4 according to the upper scale on the abscissa. M′ in c.g.s. units is of course the mass transport of silica per second through a square centimeter of cross section where the concentration drops from saturation to zero in one centimeter. For a system more nearly approaching ordinary geologic magnitudes the mass transport per year through a square meter with a gradient from saturation to zero concentration in one meter is given in column 9 of table 1 and shown graphically according to the lower scale on the abscissa of figure 4. It is seen that the mass transport ranges up to several kilograms per year, and it is evident that where thousands to hundreds of thousands or millions of years are available mass transport in supercritical water vapor can be of very great geologic magnitude, even with concentration gradients much smaller than have been assumed here.

Another value which gives some idea of the magnitude of diffusion is the so-called mean square displacement, x.

$$(10) \qquad x^2 = 2Dt$$

x is the distance from an interface in a diffusion medium at which the concentration of a solute will reach one half its concentration at the interface in time t. Values for x where t = 1 year are given in column 10 of table 1 and shown graphically in figure 5. The data indicate that if supercritical steam comes in contact with rock materials and becomes saturated with dissolved silica, it will reach half saturation at distances of one to several meters from the rock face in a year, assuming no motion of the vapor itself; tens of meters in a hundred years, thousands of meters in a million years. Since the solubility of silica in steam is not large, little mass transport is involved in establishing the half-value for concentration at a given distance. What is indicated here is some idea of the time necessary to establish a steady concentration gradient in systems of various dimensions by diffusion in supercritical water vapor.

If the diffusivities of molecular particles in high-pressure supercritical water vapor are even crudely approximated by the Stokes-Einstein equation using the values for viscosity derived here, then it is evident that diffusion in supercritical water vapor is potentially a very rapid and large-scale process, as geologic processes go, for any substance that has appreciable solubility in steam. The Stokes-Einstein equation gives useful results for gaseous diffusion in many organic fluids, and the values obtained here for viscosity, as well as the diffusivities derived from them, bear a reasonable relationship to the experimentally investigated range of measured viscosities in steam and diffusion rates in liquid water. Consequently it seems worthwhile to give serious consideration to the geologic implications of these results.

Up to now I have not dealt with the application of diffusion in supercritical water vapor to any realistic geologic model. There may be situations in volcanic or hydrothermal vein systems where an extensive body of supercritical water vapor exists for a time in an otherwise free space. Surely, however, such situations are relatively rare and of short duration. (As a petrologist, I am inclined to look on ore deposits in general as most uncommon rocks). Probably

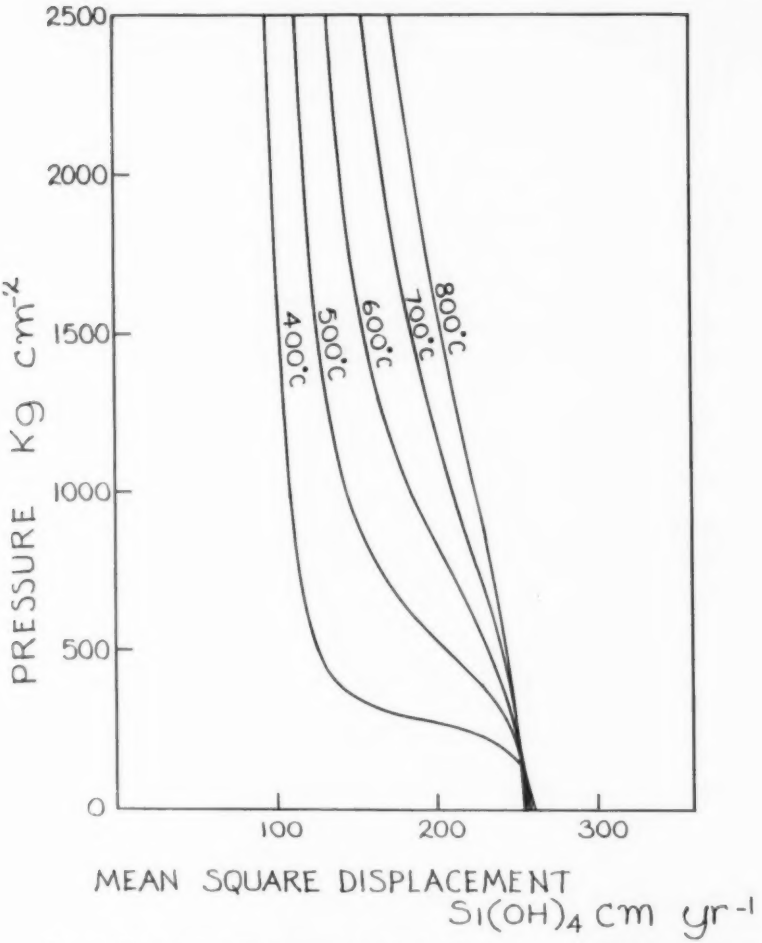

Fig. 5. Mean square displacement of silica diffusing in supercritical water vapor from a saturated interface.

supercritical water vapor most commonly exists as a porefluid or intergranular dispersed phase occupying very small free spaces in rocks. The dispersed phase may occupy such small spaces that the properties of the fluid are modified by adsorbtive forces on enclosing mineral grain surfaces. Nevertheless it is evident in many metamorphic terrains that large amounts of water have evolved from or been introduced into extensive bodies of rock. It is also evident that in the crystallization of magmas at depth, large amounts of water are evolved and react with the igneous rock and its surroundings. Korzhinsky (1936) points out

that in metasomatic processes where chemical transport is taking place throughout a body of rock, the proportion of rock that can be affected by the flow of solutions in permeable openings is very small:

> . . . the rock does not react [to a significant extent] with flowing solutions, it reacts with an immobile solution permeating the submicroscopical pores of the rock and serving as an intermediary between the whole rock mass and the flowing solutions. The introduction or leaching of rock components are affected by diffusion through this immobile subcapillary medium . . . (p. 58, English summary)

The experimental results obtained by Duffell (1937) tend to support this concept of solute transport in pore solutions.

Some rather limited but highly suggestive experiments by Garrels, Dreyer, and Howland (1949) indicate that the rate of movement of a substance through a rock by diffusion in a pore fluid is nearly independent of the fabric, so long as the rock does not interact with the diffusing substance or the properties of the fluid become modified by interaction with the pore walls. One can visualize by way of analogy an area traversed by a number of paths. The rate of speed at which one may walk is more or less fixed, so that the time used by any individual to cross the area depends only on the croookedness of the path taken. The total volume of traffic, however, in a given time is also a product of the number of available paths.

To return to Fick's equation for mass transport (7), the term A must be modified by a factor, a, less than one, which is the fraction of the average cross section occupied by effective diffusion paths. The term l must be modified by a factor, j, greater than one, which is the ratio of the average length of the diffusion paths to the straight-line distance through the rock for a given change in concentration. The equation becomes:

$$(11) \qquad m = -D\,Aa\,\frac{(\Delta C)t}{lj}$$

Garrels, et al. (1949) use a slightly different notation but in effect define $\frac{a}{j}$ as a property of any given rock which they call the effective directional porosity. It is a factor which reduces the cross section area of a rock for a given concentration gradient to the effective cross section of the free diffusion paths through the pore fluid in the rock, as though these paths were consolidated into a single hole through the rock.

To return to the diffusion of silica in supercritical water vapor, the data plotted on figure 4 indicate that hundreds to thousands of grams of silica may be transported per year through an area 1 m^2 with a concentration gradient equal to the solubility of silica at the given P and T across a distance of 1 m, if the vapor pressure of water exceeds a few hundred atmospheres and the temperature a few hundred degrees C. This means that at a surface where silica is being remorved from solution a layer of pure quartz a centimeter thick could be built up over the entire area of diffusion in a few years at commonly attained geologic pressures and temperatures. The time involved in many geologic processes such as metamorphism appears to be on the order of 10^5 or perhaps 10^6 years. Consequently the product of effective directional porosity

and concentration gradient may be reduced by corresponding orders of magnitude and still allow geologically important transport in the intergranular vapor phase.

Garrels, et al. (1949) determined a few values for effective directional porosity from measurements of diffusion in water saturated limestones at temperatures of 25 C to 65 C and got values ranging from about 0.03 to 0.8 with some indication of an increase in effective directional porosity with an increase in temperature. Duffell found measurable penetration of diffusing ions in aqueous solutions in crystalline limestones with porosities of less than one percent and little or no measurable permeability. These results can only suggest that until actual experimental measurements are made of diffusion in intergranular supercritical water vapor in rocks at temperatures and pressures in the range of metamorphic, magmatic and hydrothermal processes it would be well not to dismiss this as a transport mechanism corresponding in rate and magnitude to other major geologic transport processes.

In fact the basic diffusion rates in the vapor are so rapid that the real rate controls in the geologic realm are likely to be factors that limit effective activity gradients, or else phenomena such as adsorbtion on boundary surfaces in very small openings which modify the properties of the vapor phase. Complex coupled reactions may be involved which control the relationship of the rate at which the diffusing particle enters the vapor phase to the rate at which it is removed elsewhere in the system. The reaction at either interface may produce a product layer and diffusivity in the product layer will influence the rate of further reaction. Water in intimate contact with the surfaces of silicates tends to undergo ion exchange with the surface, hydrolizing the silicate surface and taking metal ions into solution (Stevens, 1934) (Frederickson, 1951). Ultimately a steady state tends to be reached in the pH of the water, which is always higher than 7. In capillary and subcapillary pores the base ions in solution must tend to become balanced against hydroxyl ions and more or less neutral with respect to the molecular forces in the adsorbed water skin on the surfaces. This may more than double the diffusion rates of base ions over molecular diffusion rates in neutral solutions because the mobility of hydroxyl is four or five times at great as the mobility of the ions of the common bases in rocks, and hydroxyl "drags" the metal ions along. No doubt there are other ways in which activity gradients are affected by factors other than concentration. For example, Wang (1954) has discussed an effect which reduces the activation energy of diffusion in liquid water owing to the influence on short range order in water of small surface charges on large ions or molecules in solution. This has an exponential effect on increasing diffusion rates, and may be especially important in subcapillary openings where the influence of surface charges might be large. Only empirical data can evaluate these effects.

In the meantime the calculated values given here should help to give some quantitative significance to speculations concerning the role of diffusion in high-pressure water vapor in geologic processes and perhaps serve as a guide to the design of appropriate experimental investigations of the problem.

TABLE I

1	2	3	4	5	6	7	8	9	10
T	P kg cm^{-2}	ρ gm cm^{-3}	η gm cm^{-1}sec^{-1} (Poise $\times 10^{-4}$)	Dr_s cm^{2}sec^{-1} $\times 10^{-11}$	$D_{SiO(OH)4}$ cm^{2}sec^{-1} $\times 10^{-4}$	C'_{SiO2} gm cm^{-3} $\times 10^{-4}$	M'_{SiO2} gm cm^{-1}sec^{-1} $\times 10^{-5}$	m kg	$\times$ cm per yr.
400°C (673°K)	1		F 2.33	3.18	10.67				259
	20		F 2.34	3.17	10.65				259
	40		F 2.35	3.15	10.57				258
	60		F 2.36	3.14	10.54				257
	80		F 2.38	3.10	10.40				256
	100		F 2.41	3.07	10.30				255
	200		F 2.75	2.70	9.06				239
	300	0.332		5.06	1.46	4.90	1.72	8.43	0.266	176
	400	0.513		8.49	0.87	2.92	4.05	11.83	0.373	136
	500	0.572		9.90	0.76	2.55	5.70	14.54	0.459	126
	600	0.609		10.87	0.68	2.28	7.01	15.98	0.504	120
	800	0.656		12.16	0.60	2.01	9.06	18.21	0.574	113
	1000	0.690		13.16	0.56	1.88	10.83	20.36	0.642	109
	1400	0.737		14.62	0.51	1.71	14.08	24.08	0.760	104
	2000	0.791		16.43	0.45	1.51	18.44	27.84	0.873	98
	2500	0.826		17.66	0.42	1.41				95

$\eta = (1 + 0.563d + 8.964\rho^2)2.328 \times 10^{-4}$

$b = 3.219$

TABLE 1 (Continued)

1	2	3	4	5	6	7	8	9	10
T	P kg cm^{-2}	ρ gm cm^{-3}	η gm cm^{-1}sec^{-1} (Poise $\times 10^{-4}$)	Dr_s cm^{2}sec^{-1} $\times 10^{-11}$	$Ds_{(corr)}$ cm^{2}sec^{-1} $\times 10^{-6}$	C'_{SiO_2} gm cm^{-3} $\times 10^{-4}$	M'_{SiO_2} gm cm^{-1}sec^{-1} $\times 10^{-7}$	m kg	$\times$ cm per yr.
500°C (773°K)	1		F 2.69	3.16	10.60				258
	20		F 2.70	3.15	10.57				258
	40		F 2.71	3.14	10.54				257
	60		F 2.72	3.12	10.47				257
	80		F 2.73	3.11	10.43				257
	100		F 2.75	3.09	10.38				256
	200		F 2.90	2.94	9.87				249
	300		F 3.13	2.72	9.13	0.18	1.64	0.052	240
	400	0.172	3.50	2.43	8.16	0.60	4.90	0.154	226
	500	0.249	4.22	2.01	6.75	1.59	10.73	0.338	206
	600	0.328	5.22	1.63	5.48	3.35	18.36	0.579	186
	800	0.449	7.19	1.19	4.00	8.26	33.04	1.042	159
	1000	0.523	8.68	0.98	3.29	13.26	43.63	1.376	144
	1400	0.611	10.71	0.79	2.65	22.80	60.42	1.905	129
	2000	0.691	12.82	0.66	2.21	34.91	77.15	2.433	118
	2500	0.733	14.05	0.61	2.04				114

$b = 2.88$

$\eta = (1 + 0.504\rho + 7.172\rho^3)\,2.689 \times 10^{-4}$

TABLE 1 (Continued)

1	2	3	4	5	6	7	8	9	10
T	P kg cm^{-2}	ρ gm cm^{-3}	η gm cm^{-1}sec^{-1} (Poise $\times 10^{-4}$)	Dr_s cm^{2}sec^{-1} $\times 10^{-11}$	$D_{B(OH)4}$ cm^{2}sec^{-1} $\times 10^{-4}$	C'_{SiO2} gm cm^{-3} $\times 10^{-4}$	M'_{SiO2} gm cm^{-1}sec^{-1} $\times 10^{-5}$	m kg	$\times$ cm per yr.
600°C (873°K)	1		F 3.06	3.14	10.54				257
	20		F 3.07	3.12	10.47				257
	40		F 3.08	3.11	10.43				257
	60		F 3.09	3.10	10.40				256
	80		F 3.10	3.10	10.40				256
	100		F 3.11	3.09	10.38				256
	200		F 3.20	3.00	10.06				252
	300		F 3.33	2.88	9.67	0.21	2.03	0.064	247
	400	0.121		3.50	2.74	9.20	0.64	5.89	0.186	241
	500	0.160		3.75	2.56	8.60	1.36	11.70	0.369	233
	600	0.202		4.07	2.35	7.89	2.43	19.17	0.605	223
	800	0.290		4.96	1.94	6.51	5.68	36.98	1.165	203
	1000	0.368		5.98	1.61	5.41	10.53	56.97	1.797	184
	1400	0.482		7.87	1.22	4.10	23.71	97.21	3.065	160
	2000	0.596		10.22	0.94	3.15	46.06	145.09	4.575	141
	2500	0.651		11.52	0.83	2.78				133

$\eta = (1 + 0.454\rho_r + 5.834\rho_r^3)3.058 \times 10^{-4}$

$b = 2.597$

TABLE 1 (Continued)

1	2	3	4	5	6	7	8	9	10
T	P kg cm^{-2}	ρ gm cm^{-3}	η gm cm^{-1}sec^{-1} (Poise $\times 10^{-4}$)	Dr_s cm^{2}sec^{-1} $\times 10^{-11}$	$D_{SiO(OH)_4}$ cm^{2}sec^{-1} $\times 10^{-4}$	C'_{SiO_2} gm cm^{-3} $\times 10^{-4}$	M'_{SiO_2} gm cm^{-1}sec^{-1} $\times 10^{-5}$	m kg	$\times$ cm per yr.
700°C (973°K)	1		F 3.48	3.08	10.32				255
	20		F 3.48	3.08	10.32				255
	40		F 3.49	3.07	10.30				255
	60		F 3.50	3.06	10.26				254
	80		F 3.50	3.06	10.26				254
	100		F 3.52	3.04	10.20				253
	200		F 3.58	2.99	10.03				252
	300		F 3.66	2.92	9.80				249
	400	0.098	3.77	2.84	9.54				245
	500	0.127	3.92	2.73	9.16				240
	600	0.155	4.09	2.62	8.80				237
	800	0.216	4.55	2.35	7.89				223
	1000	0.276	5.10	2.10	7.05				210
	1400	0.382	6.39	1.67	5.61				188
	2000	0.498	8.22	1.30	4.37				166
	2500	0.570	9.56	1.12	3.76				154

$b = 2.322$

$\eta = (1 + 0.3064\rho + 4.665\rho^3)3.48 \times 10^{-4}$

Table 1 (Continued)

1	2	3	4	5	6	7	8	9	10
T	P kg cm^{-2}	ρ gm cm^{-3}	η gm cm^{-1}sec^{-1} (Poise $\times 10^{-4}$)	Dr_s cm^{2}sec$^{-1} \times 10^{-11}$	$D_{Si(OH)_4}$ cm^{2}sec^{-1} $\times 10^{-5}$	C'_{SiO_2} gm cm$^{-3} \times 10^{-4}$	M'_{SiO_2} gm cm^{-1}sec^{-1} $\times 10^{-5}$	m kg	$\times$ cm per yr.
800°C (1073°K)	1		F 3.87	3.05	10.23				254
	20		F 3.88	3.05	10.23				254
	40		F 3.88	3.04	10.20				253
	60		F 3.89	3.03	10.17				253
	80		F 3.90	3.03	10.17				253
	100		F 3.91	3.02	10.13				253
	200		F 3.96	2.98	10.00				251
	300		F 4.03	2.93	9.84				249
	400	0.085	4.10	2.88	9.67				246
	500	0.108	4.20	2.81	9.43				244
	600	0.131	4.32	2.73	9.16				240
	800	0.179	4.62	2.56	8.59				233
	1000	0.226	4.97	2.37	7.96				224
	1400	0.314	5.83	2.03	6.81				207
	2000	0.419	7.15	1.65	5.54				187
	2500	0.493	8.28	1.42	4.74				173

$b = 2.132$

$\eta = (1 + 0.3731\rho + 3.9319\rho^2)3.87 \times 10^{-4}$

(F, values from Fano, et al., 1956)

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STABILITY OF SOME CARBONATES AT 25°C AND ONE ATMOSPHERE TOTAL PRESSURE*

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ABSTRACT. The stabilities of a number of carbonates, both minerals and synthetic compounds, were determined by dissolving them in water saturated with one atmosphere carbon dioxide at 25°C and one atmosphere total pressure. The pH of the solution was monitored continuously and the equilibrium value determined by extrapolating the pH-time data to infinite time. This equilibrium pH value was used to obtain the standard free energies of formation of the carbonates. The values obtained are listed below, and are compared, where data are available, with values listed in U. S. Bureau of Standards Circular 500 or in Latimer's "Oxidation Potentials."

Carbonate	$\Delta F_{f}^{\circ}{}_{298^{\circ}K}$ This work	U. S. Bureau of Standards
Calcite, natural and synthetic	-269.8_{0}	-269.78
Magnesite		-246.
Dolomite	-520.0_{0}	
Huntite	-1007.7_{0}	
Hydromagnesite	-1108.3_{0}	
Rhodochrosite, natural	-195.7	-195.4[1]
Rhodochrosite, synthetic pptd.	-194.7	-194.3 (Latimer)
Kutnahorite	-466.2	
Aragonite	-269.6_{5}	-269.53
Witherite	-272.0_{4}	-272.2
Alstonite	-543.0_{6}	
Barytocalcite	-542.9_{1}	
Strontianite, natural and synthetic	-272.0_{2}	-271.9

The value obtained for dolomite indicates that dolomite is stable with respect to calcite plus magnesite; conflicting experimental results by previous workers apparently are explained by the greatly increased solubility of dolomite that results from prolonged grinding.

INTRODUCTION

One of the oldest methods of determining the solubility of a carbonate is to dissolve it in a water solution under a fixed pressure of carbon dioxide. The justification for reporting the present work comes from the use of continuous recording of pH of the solution, which provides data that can be used to obtain accurate equilibrium values by appropriate extropolation. Equilibrium was approached at 25°C. and one atmosphere pressure only from undersaturation; but the values we obtained agree well with previous determinations in which equilibrium was approached from both sides. If the approach to equilibrium from undersaturation alone is valid, the stability of a number of species such as dolomite and huntite can be determined, even though these compounds have not yet been synthesized at room temperature and pressure.

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[1] Natural or synthetic not specified.

The method used has the additional virtue of being rapid and simple; 24 hours is usually sufficient to obtain data for determination of an equilibrium constant.

EXPERIMENTAL

Materials.—Water was prepared by distillation in a Barnstead still, and yielded a pH of 7.0 ± 0.1 after washing with nitrogen. Carbon dioxide was obtained from a commercial tank, and was bubbled through a gas-washing bottle containing distilled water to presaturate it with water before it entered the experimental container. Nitrogen, used for removing other gases from the water, was obtained from commercial tanks, and was passed through a carbon dioxide absorbent and through distilled water before use. The carbonate compounds were either mineral specimens of good quality or *Reagent Grade* commercial products (table 1). We are indebted to C. Frondel and C. Hurlbut of the Department of Mineralogy, Harvard University, for most of the specimens, Jun Ito, of the same Department, for analyses of magnesite, huntite, and dolo-

TABLE 1

Data on carbonate specimens studied

Specimen	Identification*	Analysis sample	Locality
Calcite Natural	H.M. 87189		Iceland
Calcite** Synthetic	Baker# Lot No. 11246	Same lot	
Dolomite	H.M. 105064	Same sample	Oberdorf, Styria, Austria
Huntite**	H.M. 106304	Same locality	Tea Tree Gully, S. Australia
Huntite**	H.M. 106589	Same locality	Crestmore, California
Magnesite	H.M. 105090	Same sample	Oberdorf, Styria, Austria
Hydromagnesite**		None	Soda Springs, Idaho
Rhodochrosite Natural	H.M. 96030	Same locality	John Reed Mine, Alicante, Colo.
Rhodochrosite Natural	H.M. 89794	Same specimen	Franklin, N. J.
Rhodochrosite** Synthetic	Baker Lot No. 90504	Same lot	
Rhodochrosite** Synthetic		Made from analytical grade reagents	
Kutnahorite	H.M. 85670	Same sample	Franklin, N. J.
Aragonite	H.M. 84357		Bilin, Bohemia
Alstonite	H.M. 76361	Same locality	Alston Moor, England
Barytocalcite	H.M. 80399		Alston Moor, England
Witherite	H.M. 88199		Northumberland, England
Strontianite Natural	H.M. 93448		Ahlen, Westphalia
Strontianite Synthetic	Baker Lot No. 8040	Same lot	

* H.M. = Harvard Museum

\# Baker Chemical Company, Phillipsburg, New Jersey

** Less than 2 microns

mite. Donald L. Graf of the Illinois Geological Survey gave us hydromagnesite. Analyses of the other carbonates are quoted from the literature; in a few instances they represent analyses of the same specimen, but some of the quoted analyses are of other specimens from the same locality (table 2). With the exceptions of huntite, hydromagnesite, and the synthetic materials, all of the samples used were selected from good quality, coarsely crystallized specimens. X-ray diffractometer charts were made of all the samples used, and all were found to be pure phases, properly labeled, except for the huntite specimen from Crestmore, California, which was found to be about half huntite and half aragonite.

TABLE 2

Analyses of minerals and synthetic materials used

	dolomite H.M. 105064 anal: J. Ito	magnesite H.M. 105090 anal: J. Ito	rhodochrosite Colorado Wherry & Larsen, 1917	rhodochrosite H.M. 89794 Frondel, 1955	kutnahorite H.M. 85670 Frondel, 1955
CaO	30.43	0.10	0.28	2.08	27.44
MgO	21.78	47.34	0.33	0.69	2.21
MnO	0.02	0.05	59.11	58.27	28.31
FeO	0.08	0.52	1.16	0.27	0.50
CO_2	47.37	51.88	37.89	38.71	41.80
insol.	0.44		0.82		
Total	100.12	99.89	99.59	100.02	100.26

	huntite Australia Skinner, 1958	huntite Australia Skinner, 1958	huntite H.M. 106589 anal: J. Ito		alstonite Alston, Eng. Kreutz, 1905
CaO	16.0	15.6	15.84	CaO	17.60
MgO	34.4	33.2	33.42	SrO	4.25
ign. loss			46.37	BaO	48.54
CO_2	50.4	48.9		CO_2	29.41
Cl_2	tr	N.D.			
Fe, Al			small		
insol.	nil	N.D.	3.95		
Total	100.8	97.7	99.58	Total	99.80

	Synthetic Calcite Baker Lot #14246	Synthetic Rhodochrosite Baker Lot #90504	Synthetic Strontianite Baker Lot #8040
insoluble in HCl		0.010	
chloride		0.010	0.002
sulfate		0.003	0.003
nitrate			0.010
iron		0.002	0.001
other heavy metals (as Pb)		0.005	
barium	<0.01		0.002
zinc		0.05	
Mg and alkali salts (as SO_4)	0.052	0.12	0.022

The mineral specimens were ground dry in a motor-driven agate mortar before they were dissolved; most synthetic carbonates were sufficiently fine as obtained to give satisfactorily high solution rates. No attempt was made to size the ground carbonates; in general all material used was less than 0.1 mm.

Apparatus.—Solution of the carbonates was carried out in cylindrical pyrex containers of 600 ml capacity. Covers for the containers were made from 1/4 inch thick plastic plate, cut to fit, and having holes to fit #3 and #1 rubber stoppers. Communication with the solution was established by means of a set of pH-measuring electrodes mounted in rubber stoppers and inserted through the holes in the cover. A resistance thermometer for temperature compensation, a platinum electrode for solution grounding, and a gas inlet tube were also introduced through rubber stoppers firmly seated in the holes in the plastic cover. Leads from the electrodes, thermal compensator, and solution ground were connected to an amplifier and an automatic recorder. In order to use a magnetic stirrer the water bath was set upon the stirring motors and the reaction vessels were wrapped in flexible plastic material and sunk to the bottom of the bath. Thus a seal became unnecessary, because the plastic envelope, which stretched about 12 inches above the top of the container, soon became filled with whatever gas was fed in, and provided the desired pressure of one atmosphere. Most experiments were run in duplicate; the pH of each container was recorded every 18 seconds. The apparatus used is well balanced for measurements of pH to within 0.01 pH units; we estimate the accuracy of individual measurements as about $\pm$ 0.02 pH units. The temperature of the water bath was controlled at 25 $\pm$ 0.1°C.

Procedure.—The electrodes were first calibrated in pH 7 and pH 4 standard buffer solutions; the check was always within 0.01 pH units. Then the pyrex container and electrodes were carefully cleaned and 500 ml of distilled water added. A teflon coated magnetic bar was used to stir the solution. Then, if the hydrolysis (i.e., carbonate and water with no CO_2 gas) pH was to be measured, the water was washed with N_2 to a pH of 7.0 $\pm$ 0.1. Finally several grams of fine grained carbonate were added. The container was encased in the plastic envelope, weighed down, sunk to the bottom of the water bath, and stirred continuously through the glass bottom of the bath. Then CO_2 was bubbled continuously through the solution. The pH, originally high as a result of the hydrolysis of the carbonate, dropped rapidly to a low value, then started to rise again as the carbonate dissolved. Several runs in the absence of carbonate showed that the water quickly became saturated with CO_2, and gave pH values consistent with equilibrium between gas and solution (pH = 3.91).

No attempts were made to compensate for variations in atmospheric pressure, and hence CO_2 pressure in the solution. Records of barometric pressure during the experiments, obtained from the U. S. Weather Bureau, showed that the variations from one atmosphere were not sufficient to affect our calculations.

The pH values obtained during each run were plotted on linear or semi-log paper against time$^{-1/2}$ to obtain an extrapolation to an equilibrium value at infinite time. These plots were empirically chosen because they yielded nearly linear plots as equilibrium was approached.

After a given pair of samples had run long enough to give a satisfactory approach to equilibrium, stirring was stopped, and the supernatant solution and suspended carbonate removed by decanting. Fresh water was added, and the run repeated. This procedure was used to avoid the possibility of a significant contribution to the solubility from material so fine grained as to have a significantly higher surface energy than bulk material.

Most runs required 12 to 18 hours under these experimental conditions. When some of the more slowly soluble carbonates required more time, we tried to bring them back into the 12 to 18 hour range by using larger samples or finer grinding, or both. If the runs lasted 3 or 4 days, contamination of the solution and of the calomel electrode resulted, and there was difficulty in obtaining checks on buffer solutions. Also, diffusion of KCl from the calomel electrode caused an unknown increase in ionic strength of the solution.

Analyses of solutions that had approached equilibrium were made from time to time to check calculated values. The concentration of bicarbonate ion was determined by titrating the filtered solution with standard HCl under one atmosphere CO_2 to an endpoint at pH 3.91. Calcium was determined by precipitation as the oxalate, or calcium and magnesium were determined by titration with Versene, according to the procedure outlined by Shapiro and Brannock (Shapiro and Brannock, 1956). Barium was determined gravimetrically as the sulfate, and manganese colorimetrically after oxidation to permanganate. The results are discussed under the sections devoted to the behavior of the individual carbonates.

RESULTS

General.—Typical results of the experiments are shown in figure 1. Figure 1a shows curves for huntite and calcite. The similarity in behavior indicates that a similar solution mechanism is involved, despite the fact that huntite contains two different essential cations. Complete equilibrium was seldom achieved, but figure 1b, which shows data for synthetic $SrCO_3$, il-

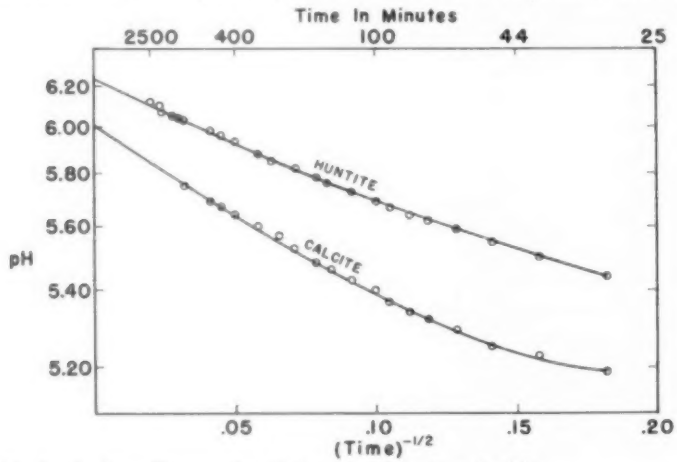

Fig 1. A. Log pH versus time$^{-1/2}$ for runs of huntite and calcite.

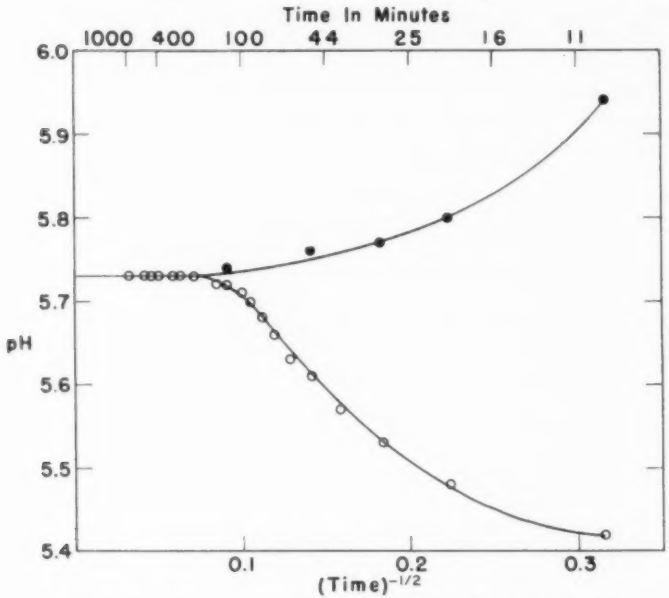

Fig. 1. B. pH versus time$^{-1/2}$ for two runs of synthetic strontianite.

lustrates achievement of equilibrium during the experiment. It would be expected, therefore, that our extrapolated equilibrium values from runs of the type shown in figure 1a would give a pH that is too high, and from this a lower than actual stability. However, our experimental points are sufficiently close to the ordinate to preclude the possibility of a serious error. Also, comparison of our results with those of previous investigators shows that our deviation from them is in the direction of greater, rather than lesser, stability.

Calcite.—Both natural and synthetic calcites were run. The natural material was large clear rhombic cleavage fragments of Iceland spar. Synthetic calcite, obtained from D. Stewart of the U. S. Geological Survey, was a specimen of reagent grade material produced by J. T. Baker Chemical Company. Both the natural and synthetic calcite dissolved very rapidly, and a value for the equilibrium pH accurate within 0.01 or 0.02 pH units could be taken from the highest pH achieved in most of the runs. The filtered solution from some of the runs, left open to the room so that the CO_2 might pass off, precipitated a mixture of calcite and aragonite. Equilibrium pH is 6.02.

Magnesite.—The magnesite used was unusually pure material, as shown by the analysis in table 2, but a reliable extrapolation to equilibrium pH was not obtained because the mineral dissolved so slowly that the curves approached the "infinity axis" much too steeply. Numerous runs, using up to 30 grams of finely ground magnesite, were made, with inconclusive results. The filtered outgassed solutions formed no precipitate for months, until, because of evaporation, nesquehoneite, $MgCO_3.3H_2O$ formed. A cleavage fragment of magnesite,

suspended in one such solution for 18 days, showed no gain or loss of weight. No satisfactory equilibrium pH was obtained.

Dolomite.—The dolomite specimen used was also of very pure material (see analysis in table 2). Unlike the magnesite from the same locality, however, dolomite behaved very well when subjected to our standard procedure. Good duplication of results was obtained, even from the earliest runs, made outside the water bath. However, if a run was allowed to approach to within about 0.1 pH units of the extrapolated equilibrium value (fig. 2), and then subjected to the addition of several grams of dolomite that had been ground for 12 hours or more, the pH rose rapidly, and leveled off to give an extrapolated value appropriate to aragonite. When this experiment was re-run, after

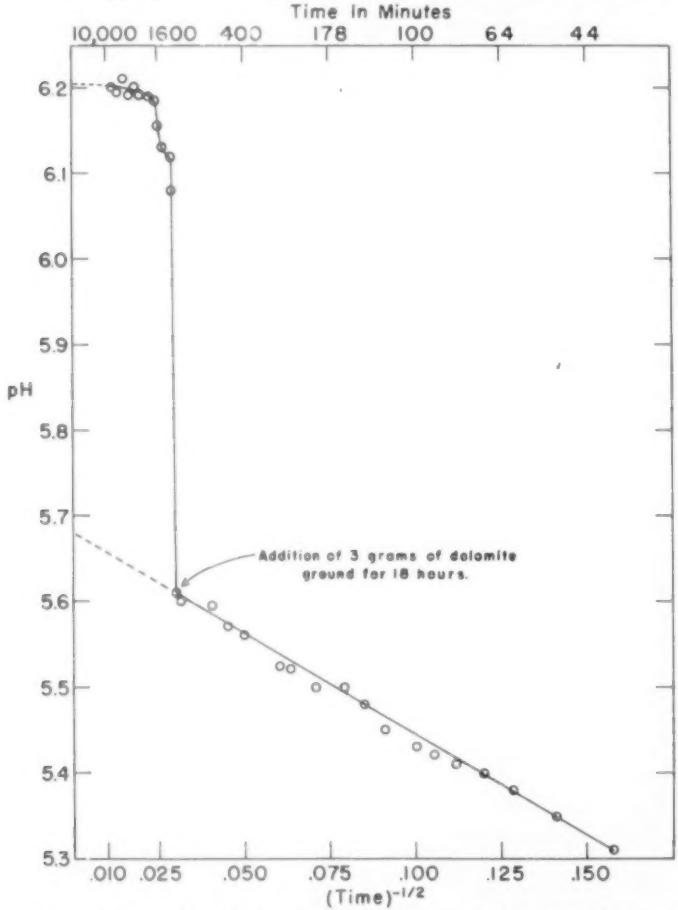

Fig. 2. Effect of adding finely ground dolomite to a solution approaching saturation with coarser material.

removing the supernatant liquid and its accompanying fine particles, an extrapolation to the usual pH was obtained. Equilibrium pH (coarse material) is 5.68.

Huntite.—Two specimens of huntite were run, but that from Crestmore was found to be a mixture of about equal proportions of aragonite and huntite. That from Australia was a single phase, however, and good duplication of results was obtained from it. Moreover, analyses of some of the solutions showed that the mineral dissolved essentially congruently. However, we cannot be sure that huntite is as stable as calculated; it is possible that it dissolved congruently until calcite started to precipitate, and then ceased reacting. The precipitate that formed when some of the filtered solution was left open to the room was calcite.

The runs of the Crestmore aragonite-huntite showed an interesting break in slope, from which two extrapolations might be made—the lower one to approximately the equilibrium pH of aragonite, and the upper to about the equilibrium pH of huntite. Equilibrium pH is 6.24.

Hydromagnesite.—The hydromagnesite specimen, from near Soda Springs, Idaho, was not analyzed chemically, but the x-ray diffractometer chart showed it to consist essentially of hydromagnesite, with no other carbonates present, but with 10 or 15 percent of silt and clay. Two runs of this material gave duplicate results, but the standard HCl titrations of the solutions did not confirm the measured pH's. It may be that at pH's of 6 or higher, the Mg^{++} ion is partially complexed, and the measured pH does not give a true measure of the cation concentration. Comparison of a series of calculated versus measured bicarbonate molalities for magnesium bicarbonate solutions indicate the presence of a minor amount of associated $Mg(HCO_3)_2$ or $Mg(HCO_3)^+$. We regard the equilibrium constant value for hydromagnesite as the least reliable of the listed values. Equilibrium pH value is 6.71.

Rhodochrosite.—Two mineral specimens of rhodochrosite were run; both contained about 5 mole percent of other cations in diadochic substitution. Good extrapolations to an equilibrium pH were not easily obtained from either rhodochrosite, so the average result of a number of runs is presented. Precipitated $MnCO_3$, prepared from Reagent Grade reagents, was shown by the x-ray diffractometer to have the structure of rhodochrosite, though the reflections were broad. This material was found to be more soluble than the mineral rhodochrosites. As differences in solubility were not found between other mineral and synthetic carbonate pairs, it may be that the difference found for $MnCO_3$ is due to the presence of about 5 mole percent of other cations in the natural rhodochrosites. A small amount of better crystallized synthetic rhodochrosite was made by using an electric current to cause reaction of Mn^{++} and HCO_3^- ions in a salt bridge. The rate of precipitation was necessarily slow, and only about 100 mg were obtained. (The reaction between Mn^{++} and HCO_3^- produces CO_2 as well as $MnCO_3$, but the side effect of oxidation of Mn^{++} is less at the lower pH of the HCO_3^- solution than at that of the higher pH of a CO_3^{--} solution.) One equilibrium pH run only was made with this material because so little was available, and a projected equilibrium pH value of 5.73 was obtained. Equilibrium pH of natural rhodochrosite is 5.09; of fine grained precipitated $MnCO_3$ is 5.35.

Kutnahorite.—Our sample of kutnahorite was part of an analyzed specimen from Franklin, New Jersey. The x-ray diffractometer chart of our sample showed only kutnahorite peaks, but the solution behavior suggested that it might be contaminated with a little calcite, or perhaps the grinding involved in the preparation of the sample tended to disorder the cations. The first few runs projected to and reached considerably higher pH's than later runs. The filtered solution from one of the later runs was titrated with standard acid, and confirmed the measured pH exactly. The colorimetric analysis showed that Mn was 49.5 mole percent of the total cations. Equilibrium pH is 5.58.

Aragonite.—The aragonite sample was prepared from beautifully crystallized material from Bilin, Czechoslovakia. Two runs were made, giving good duplication of results, and checking the Bureau of Standards value very closely. Equilibrium pH is 6.08.

Witherite.—The sample of witherite was prepared from one large crystal. Two runs were made, giving good duplication, and titration of the solution for HCO_3^- and precipitation of Ba as the sulfate both confirmed the measured pH. Witherite precipitated again from the filtered solution. Equilibrium pH is 5.93.

Alstonite.—The alstonite sample was prepared by handpicking to separate it from the associated calcite and witherite. Most of the fragments of alstonite were recognized by their distinctive crystal habit, as well as by distinctive luster. The x-ray diffractometer chart showed no extra peaks. Three runs were made, giving reasonably good duplication. Titration of one of the solutions for HCO_3^- confirmed the measured pH. The phase that precipitated out of one of the filtered solutions was a barian calcite. Equilibrium pH is 5.93.

Barytocalcite.—This sample was also prepared by handpicking from the associated barite and calcite. The barytocalcite was recognized by a difference in luster. The x-ray diffractometer chart showed no extra peaks. Two runs were made, giving reasonably good duplication.

The precipitate that formed in a filtered solution of barytocalcite was a barian calcite that was found by analysis to contain 40 mol percent $BaCO_3$. Equilibrium pH is 5.95.

Strontianite.—Both natural and synthetic strontianites were run, and good agreement was obtained between the coarsely crystallized mineral and the fine grained synthetic precipitate. Titrations for HCO_3^- confirmed the measured pH's, and the phase that precipitated from the filtered solution was again strontianite. Equilibrium pH is 5.73.

Summary.—The equilibrium pH values for the carbonates, as well as their dissociation constants, are summarized in table 3 and figure 3. In the figure, equilibrium constants for all carbonates are shown on the basis of dissociation to a single carbonate ion (e.g. k dolomite $= a^{1/2}_{Mg^{++}} a^{1/2}_{Ca^{++}} a_{CO_3^{--}}$). The position of a given carbonate in the table is a criterion of its stability in aqueous solution in the absence of complexing agents.

DISCUSSION OF RESULTS

Standard free energy values.—The equilibrium constants for the ionization of the carbonates, and hence their standard free energies of formation from the elements at 25°C and 1 atmosphere total pressure can be obtained

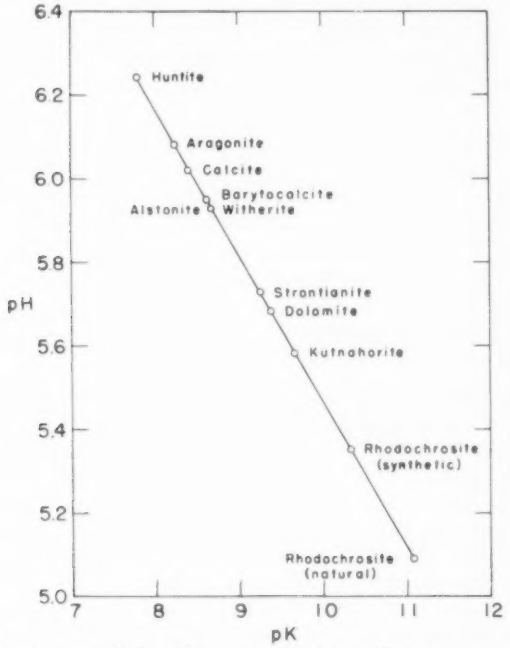

Fig. 3. Equilibrium pH for solutions saturated in carbonate compounds versus dissociation constant of solid carbonate, 25°C and 1 atmosphere CO_2 pressure.

from the equilibrium pH values. The calculations depend upon ΔF_f° values already available in the literature for various ionic and molecular species, so that the values obtained for the carbonates are no better than the other data used.

TABLE 3

Equilibrium pH values for carbonate species

Equilibrium pH	Species
5.09	rhodochrosite, Colo.
5.09	rhodochrosite, N. J.
5.35	syn. $MnCO_3$
5.58	kutnahorite
5.70	dolomite
5.73	strontianite
5.73	syn. $SrCO_3$
5.93	witherite
5.93	alstonite
5.95	barytocalcite
6.02	calcite
6.02	syn. $CaCO_3$
6.08	aragonite
6.24	huntite, Australia
6.71	hydromagnesite

A sample calculation for dolomite should suffice to show the procedure used in obtaining ΔF_f° values.

For the dissociation of dolomite, $CaMg(CO_3)_2 = Ca^{++} + Mg^{++} + 2CO_3^{--}$, the equation for the solubility product, K, is:

$$K = a_{Ca^{++}} a_{Mg^{++}} a^2_{CO_3^{--}} \quad (1)$$

The value for $a_{CO_3^{--}}$ is obtained from the equilibrium pH through the following relationships from the equilibrium for carbonic acid (Harned and Owen, 1958).

$$P_{CO_2} / a_{H_2CO_3} = 10^{+1.47} \quad (2)$$

$$a_{H^+} a_{HCO_3^-} / a_{H_2CO_3} = 10^{-6.35} \quad (3)$$

$$a_{H^+} a_{CO_3^{--}} / a_{HCO_3^-} = 10^{-10.33} \quad (4)$$

Combining equations #2 and #3, and setting $P_{CO_2} = 1$:

$$a_{HCO_3^-} = 10^{-6.35} \times 10^{-1.47} / a_{H^+} = 10^{-7.82} / a_{H^+} \quad (5)$$

The values for $a_{Ca^{++}}$ and $a_{Mg^{++}}$ are also obtained from the equilibrium pH, though less directly. When dolomite dissolves to equilibrium in water saturated with CO_2 at one atmosphere pressure:

$$CaMg(CO_3)_2 + 2H_2O + 2CO_2 = Ca^{++} + Mg^{++} + 4HCO_3^- \quad (6)$$

At the pH values (5-7) found experimentally[2], no dissolved ionic species other than Ca^{++}, Mg^{++}, and HCO_3^- need be considered as being of quantitative importance in the mass balance, hence a close approximation is:

$$2m_{Ca^{++}} + 2m_{Mg^{++}} = m_{HCO_3^-} \quad (7)$$

Because dolomite apparently dissolves congruently (the ion products of Ca^{++} or Mg^{++} times CO_3^{--} are less than those for any other known solid carbonate species):

$$m_{Ca^{++}} = m_{Mg^{++}} = 1/4 m_{HCO_3^-} \quad (8)$$

If the ionic strength is known, then ionic activity coefficients (γ) may be calculated and the value for $a_{HCO_3^-}$ from equation #5 may be converted to $m_{HCO_3^-} \cdot m_{HCO_3^-}$, in equation #8, yields values for $m_{Ca^{++}}$ and $m_{Mg^{++}}$, which are in turn converted to $a_{Ca^{++}}$ and $a_{Mg^{++}}$. The equation for ionic strength is:

$$\mu = 1/2 \, \Sigma m_i z_i^2 \quad (9)$$

Again, the only quantitatively important species in the solution are the dissolved cations and HCO_3^-. Therefore, in the case of dolomite:

$$\mu = 1/2 \, (4m_{Ca^{++}} + 4m_{Mg^{++}} + m_{HCO_3^-}) \quad (10)$$

In general, for doubly charged cations, the expression for μ is reducible to:

$$\mu = 1/2 \, (3m_{HCO_3^-}) \quad (11)$$

Using the value for μ in the Debye-Hückel equation, (Klotz, 1950)

$$-\log \gamma_i = A z_i^2 \sqrt{\mu} / (1 + a^\circ B \sqrt{\mu}) \quad (12)$$

values for $\gamma_{HCO_3^-}$, $\gamma_{Ca^{++}}$, and $\gamma_{Mg^{++}}$ are obtained.

An analytical determination of $m_{HCO_3^-}$ may be made by titrating the solution with a standard acid, but in general $m_{HCO_3^-}$ was calculated from $a_{HCO_3^-}$

[2] At higher pH values the approximation given by (7) is not so close.

by a method of successive approximations. For the first approximation $a_{HCO_3^-}$ is assumed to be equal to $m_{HCO_3^-}$. From this, ionic strength and $\gamma_{HCO_3^-}$ are calculated. Then $\gamma_{HCO_3^-}$ is used to correct $a_{HCO_3^-}$ and new values for ionic strength and $\gamma_{HCO_3^-}$ are calculated. In most cases it is necessary to repeat this cycling only two or three times. An example of the calculation for dolomite is given. To simplify the calculations γ's are read from a previously prepared graph of γ_i versus μ taken from a table in Klotz (p. 332).

Sample calculation.—Equilibrium pH for dolomite = 5.68 (table 3).

$$a_{HCO_3^-} = 10^{-7.82}/a_{H^+} = 10^{-7.82}/10^{-5.68} = 10^{-2.14} = 0.00724$$

$$m_{HCO_3^-} = a_{HCO_3^-} = 0.00724 \text{ (First approximation)}$$

$$\mu = 3/2\ (0.00724) = 0.01084$$

$$\gamma_{HCO_3^-} = 0.902$$

$$m_{HCO_3^-} = a_{HCO_3^-}/.902 = 0.00724/.902 = 0.00802 \text{ (Second approximation)}$$

$$\mu = 3/2\ (0.00802) = 0.01202$$

$$\gamma_{HCO_3^-} = 0.898$$

$$m_{HCO_3^-} = 0.00724/.898 = 0.00805 \text{ (Third approximation)}$$

$$\mu = 3/2\ (0.00805) = 0.01208$$

$$\gamma_{HCO_3} = 0.898$$

$$m_{Ca^{++}} = m_{Mg^{++}} = 1/4\ m_{HCO_3^-} = 0.00201$$

$$\gamma_{Ca^{++}} = 0.654$$

$$\gamma_{Mg^{++}} = 0.665$$

$$a_{Ca^{++}} = (0.00201)\ .654 = 0.00131 = 10^{-2.88}$$

$$a_{Mg^{++}} = (0.00201)\ .665 = 0.00135 = 10^{-2.87}$$

$$a_{CO_3^{--}} = \frac{10^{-10.33} \times 10^{-2.14}}{10^{-5.68}} = 10^{-6.79}$$

$$K = (10^{-2.88})(10^{-2.87})(10^{-6.79})^2 = 10^{-19.33}$$

From the relation $\Delta F_R^\circ = -RT \ln K = -1.364 \log k$ at 25°C and 1 atmosphere pressure, the standard free energy of reaction 9 is:

$$\Delta F_R^\circ = -1.364 \times -19.33 = 26.37 \text{ kilocalories} \qquad (13$$

Then we can write:

$$\Delta F_R^\circ = \Delta F_{f\ Ca^{++}}^\circ + \Delta F_{f\ Mg^{++}}^\circ + 2\Delta F_{f\ CO_3^{--}}^\circ - \Delta F_{f\ CaMg(CO_3)_2}^\circ$$

Substituting the value for ΔF_R° obtained in equation 13, and values for the ions from U. S. Bureau of Standards Circular 500:

$$+26.37 = -132.18 - 108.99 - 252.44 - \Delta F_{f\ CaMg(CO_3)_2}^\circ$$

$$\Delta F_{f\ CaMg(CO_3)_2}^\circ = -519.9_8 \text{ kilocalories}$$

A check on the consistency of the free energy values from the literature can be obtained by calculating ΔF_f° dolomite from the initial reaction with CO_2:

$$CaMg(CO_3)_2 + 2H_2O + 2CO_2 = Ca^{++} + Mg^{++} + 4HCO_3^-$$

$$K = 10^{-14.31}$$

$$\Delta F_R^\circ = +19.52 \text{ kcal.}$$

$$+19.52 = \Delta F_{f\ Ca^{++}}^\circ + \Delta F_{f\ Mg^{++}}^\circ + 4\Delta F_{f\ HCO_3^-}^\circ - \Delta F_{f\ CaMg(CO_3)_2}^\circ - 2\Delta F_{f\ H_2O}^\circ - 2\Delta F_{f\ CO_2}^\circ$$

$$19.52 = -132.18 - 108.99 - 561.24 - \Delta F_f^\circ{}_{CaMg(CO_3)_2} + 113.4 + 188.52$$

$$\Delta F_f^\circ{}_{CaMg(CO_3)_2} = -520.0_1 \text{ kilocalories}$$

Our estimate of the accuracy of the free energy values, based on the checks against known values where available, the consistency of values obtained by various calculation routes, the generally good agreement between analyzed solutions and values calculated for them and the probable error in determining the extrapolated equilibrium pH value, is that they are generally accurate to about ± 0.2 kilocalorie. This assumes no error in the Bureau of Standards values for various species used in calculating ΔF_f° of a given carbonate from the standard free energy of the dissociation reaction.

Relations among the Ca-Mg carbonates.—Relations among the Ca-Mg carbonates, although not entirely definitive because of our inability to get a satisfactory free energy value for magnesite, indicate that calcite and magnesite are unstable with respect to dolomite at 1 atmosphere total pressure and 25°C. Using the U. S. Bureau of Standards value for magnesite:

$$CaCO_3 + MgCO_3 = CaMg(CO_3)_2;\ \Delta F_R^\circ \cong -4 \text{ kilocalories}$$

Huntite apparently is not stable with respect to dolomite and magnesite:

$$CaMg(CO_3)_2 + 2MgCO_3 = CaMg_3(CO_3)_4;\ \Delta F_R^\circ = +5.1 \text{ kilocalories}$$

Nesquehonite is markedly unstable (Latimer, 1952). Even in the presence of pure water:

$$MgCO_3.3\,H_2O = MgCO_3 + 3\,H_2O;\ \Delta F_R^\circ = -4.5 \text{ kilocalories}$$

Thus in the composition triangle $CaCO_3$–$MgCO_3$–H_2O, relations among the species studied are shown in figure 4.

The solubility of the carbonates in water is so small that the composition of the solutions in equilibrium with the solids cannot be shown well on figure 4. A more graphic illustration of the relations in this system is obtained by plotting stability of the solids as a function of the activities of the Ca^{++} and Mg^{++} ions in solution, and as a function of P_{CO_2}. This permits inclusion of hydromagnesite, which falls outside the triangle $CaCO_3$–$MgCO_3$–H_2O.

All the reactions of interest can be written in terms of the three variables $a_{Ca^{++}}$, $a_{Mg^{++}}$, and P_{CO_2}, always assuming water in excess. For example, for equilibrium between calcite and dolomite:

$$2\,CaCO_3 + Mg^{++} = CaMg(CO_3)_2 + Ca^{++} \qquad (14)$$

$$K = \frac{a_{Ca^{++}}}{a_{Mg^{++}}}$$

For equilibrium between calcite and hydromagnesite:

$$4\,CaCO_3 + 4\,Mg^{++} + H_2O = Mg_4(CO_3)_3(OH)_2.3H_2O + 4Ca^{++} + CO_2$$

$$K = \frac{a^4_{Ca^{++}} P_{CO_2}}{a^4_{Mg^{++}}}$$

Consequently a logarithmic plot of the variables provides linear boundaries among species.

The summary diagram is shown in figure 5. Note that hydromagnesite is not stable under earth surface conditions ($P_{CO_2} = 10^{-3.5}$). Moreover, if the ratios of the molalities of Ca^{++} and Mg^{++} in sea water are used as criteria of their activities, the stable carbonate in sea water should be dolomite. In other words, the implication is that the oceans are supersaturated with respect

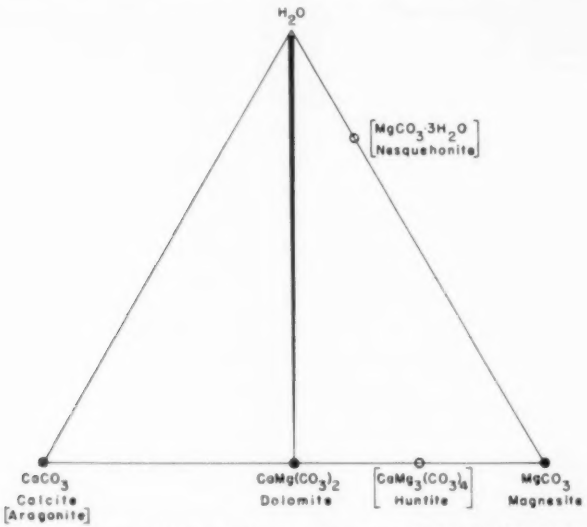

Fig. 4. Some stability relations in the system $CaCO_3$–$MgCO_3$–H_2O.

to dolomite, and calcite or aragonite on the floor of the sea should react with the sea water to form dolomite until the ratio of the activity of Ca^{++} to Mg^{++} is equal to $10^{+2.48}$.

There appear to be two alternatives to this conclusion. First, our value for the free energy of formation of dolomite may be in error. Second, the concentration of magnesium ion in sea water may be vastly different from its activity. The approximate activity of calcium ion in sea water is not in serious question,[3] therefore any large anomalies between concentrations and activities must be attributed to the magnesium ion. The small amount of indirect evidence available now suggests that the value we have obtained for the free energy of formation of dolomite is approximately correct, and that the near-absence of dolomite as a primary marine precipitate results from supersaturation.

Robie (personal communication) has summarized all the data available for calcite, magnesite, and dolomite, and has determined values for their free energies of formation that are in essential agreement with ours.

The solubility data of Yanat'eva (1954) on calcite, magnesite, and dolomite, as determined at 25°C and 1 atmosphere P_{CO_2}, show dolomite as a stable phase. On the other hand her data at 25°C, 1 atmosphere total pressure but with $P_{CO_2} = 10^{-3.5}$ (that of the present atmosphere), indicate that dolomite dissolves incongruently to yield calcite plus solution. As shown in figure 5 or in equation number 14, the stability of dolomite relative to calcite is not a function of P_{CO_2}, so the inference is that her experiments at lower P_{CO_2} and hence higher pH, somehow caused dolomite to increase its relative solubility drastically.

[3] The activity coefficient for Ca^{++} in sea water is of the order of 0.24, as shown by various studies of the solubility of calcite. (c.f. Garrels and Dreyer, 1952, p. 334.)

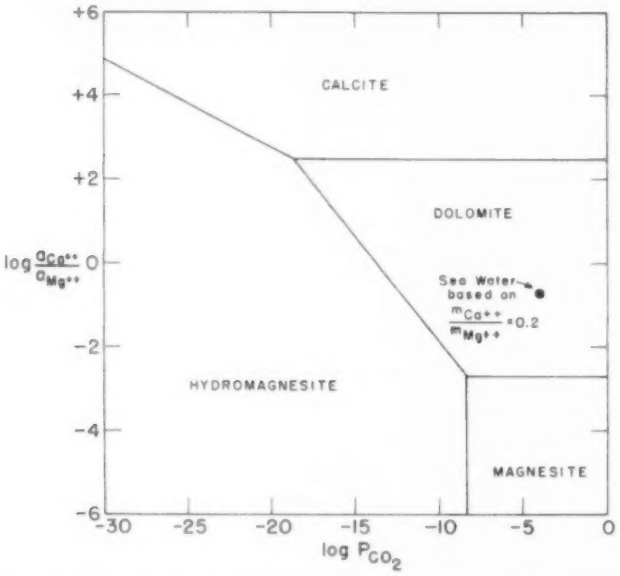

Fig. 5. Stability of some Ca-Mg carbonates in aqueous solution at 25°C. and one atmosphere total pressure, as a function of calcium-magnesium ion ratio and partial pressure of carbon dioxide.

One possible explanation of this peculiar phenomenon is that the behavior of dolomite is analogous to that of quartz. When quartz solubility is determined by experiments during which the quartz is tumbled or otherwise ground, the solubility increases by 10 to 15 times and approaches that of amorphous silica (Van Lier, 1959). This increased solubility is considered to result from the disordering of the quartz surface during grinding, so that a layer of amorphous silica is produced. Because dolomite has two structurally nonequivalent cations it is susceptible to disordering effects from grinding. This disordering has been reported by Bradley, Burst, and Graf (1953). These effects would be especially noticeable in experiments in which the dolomite would be continuously stirred or tumbled for long periods of time. The effects of a very slight disordering produced during the preparation of the sample would be noticed especially in experiments where the solubility is small, as under low CO_2 partial pressures.

To test this hypothesis we permitted dolomite to react with water saturated with CO_2 under one atmosphere pressure, until the pH of the solution was within 0.1 pH unit of the extrapolated equilibrium value. (Note that under these conditions dolomite is soluble enough so that if any small portion of it has been disordered by the original preparation of the sample it will all be dissolved before the solution is saturated.) Then three grams of the same dolomite, that had been ground continuously for 18 hours, were added to the system. The effect was immediate and striking. Within minutes the pH had

risen nearly 0.5 pH units, and after a few hundred minutes a new extrapolated equilibrium pH was obtained (fig. 2). Calculations based on the higher value (pH 6.2) show that the product $a_{Ca^{++}} \times a_{CO_3^{--}}$ is $10^{-8.22}$, exactly the value we had previously determined as the equilibrium constant for aragonite. Apparently the prolonged grinding had so increased dolomite solubility that it dissolved incongruently to yield $CaCO_3$ plus magnesium-rich solution.

It was also found that when the first solution was decanted and replaced with more distilled water and the solution experiment repeated that the dolomite had reverted to its original solubility. In other words, the material responsible for the increased solubility had all been dissolved during the first run or was carried off by the decanting, and by the time the solution approached saturation the second time, we were again measuring the solubility of relatively coarse-grained, ordered dolomite.

The anomalously high solubility was measured again by addition of more of the well-ground dolomite to the new solution, with the same results.

It is concluded that our usual procedure measures the stability of dolomite accurately, and that the higher solubilities reported by other investigators result from grinding, either during sample preparation or from the stirring or tumbling during the measurement itself.

Our experiments are too preliminary in nature to explain this phenomenon completely. One possibility is that the surfaces of the grains are disordered during prolonged grinding; another possibility is that a small amount of the sample is ground so fine that its solubility is enhanced. Ordinarily, when a supersaturated solution is in contact with the appropriate solid, the supersaturation is relieved by precipitation on the less soluble larger grains, but because of the extremely slow rate of precipitation of dolomite, this effect is probably not seen in the usual experiments. X-ray diffractometer charts of the dolomite before and after grinding showed that the prolonged grinding tended to produce line broadening due to decreased particle size. There was no apparent relative intensity decrease of the ordering reflections.

Similarly, well-ground calcite was added to a calcite run near the equilibrium pH. After the first addition the solution attained the equilibrium pH and successive additions of finely ground material raised the pH by no more than 0.01 pH units.

Within 5 minutes of each addition, the pH was again at the equilibrium value. The effect in this case is so slight that we cannot definitely say whether the small increase in pH was due to excess solubility of the finely ground material, or whether it was due to a slight loss of CO_2 atmosphere as a result of the necessary opening of the container.

Furthermore, our whole experience with magnesium ion in solution has impressed us with its reluctance to form solids from saturated solution. When solutions partly saturated with magnesite at $P_{CO_2} = 1$ atmosphere were allowed to stand open, so that the P_{CO_2} approached that of the laboratory, no precipitate formed over a period of several months. These solutions were highly supersaturated with respect to magnesite. If precipitation was finally forced by permitting the solutions to evaporate, the product was nesquehonite, which is many times as soluble as magnesite.

Perhaps the clue to the reluctance of magnesian carbonates to precipitate lies in some peculiar characteristic of the magnesium ion; it may be abnormally firmly hydrated, or it may form a stable ion pair $(MgCO_3)^\circ$.

Calcium-barium carbonates.—The data on the calcium-barium carbonate system indicates that the ordered intermediate phases barytocalcite and alstonite have approximately the same solubility, and that they are slightly more stable than an ideal solid solution of the same composition. Our data are not good enough to permit us to determine which of the dimorphs is more stable, but the free energy of the reaction

$$BaCa(CO_3)_2 \text{ (Barytocalcite)} = BaCa(CO_3)_2 \text{ (Alstonite)}$$

is probably not more than $\pm$ 100 calories. In harmony with our other attempts to form ordered intermediate phases, the precipitate resulting from loss of CO_2 from a nearly saturated CO_2-rich solution yielded a high (40 mol %) barian calcite, rather than the initial barytocalcite or alstonite.

Ca-Mn carbonates.—Results of experiments involving kutnahorite indicate that this ordered intermediate phase is stable at the conditions of the experiment. Also, we observed a marked difference in the stability of precipitated and natural $MnCO_3$. The difference we found is about the same as that reported by Latimer (Latimer, 1952, p. 235).

Sr.-carbonate.—Our value for strontianite agrees closely with that of the Bureau of Standards. No anomalies in behavior were observed.

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CLASSIFICATION OF ARENITES

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ABSTRACT. A critical examination of the classificatory schemes of Pettijohn (1954), Gilbert (1955), Packham (1954), and Folk (1954) leads to the conclusion that only Packham's, which uses sedimentary structures as a parameter, is validly based genetically. Packham's scheme is expanded by the introduction of a generalized, non-genetic, 'arenite' diagram which is congruent with the genetic graywacke and arkose-quartzose sandstone (here termed simply 'sandstone') diagrams and which enables it to deal with arenites when data on sedimentary structures are not available.

A new QFR diagram is introduced having quartz, feldspar, and rock fragments plus other labiles as parameters. The non-genetic classes of labile arenites recognized are feldspathic, lithofeldspathic, feldspatholithic, and lithic. Congruent graywacke and sandstone QFR diagrams may be employed where appropriate. Two classes of sublabile arenite are recognized—feldspathic sublabile arenite and lithic sublabile arenite. The term 'arenite' may again be replaced by 'sandstone' or 'graywacke' where appropriate. The use of 'feldspathic sandstone/arenite/wacke' as descriptive of sublabile arenites should be discontinued.

INTRODUCTION

Since the publication of Krynine's classic paper on sedimentary rock classification (Krynine, 1948), in which ternary diagrams were first utilized for classifying arenites, a number of classificatory schemes for detrital arenites have appeared. Those of Pettijohn (1949), replaced by his scheme of 1954, Gilbert (1955), Packham (1954), and Folk (1954) have found the widest acceptance, and have largely superseded Krynine's scheme. Certain shortcomings exist in each of the newer classifications, but, as will be shown, only those in Packham's can be remedied without destroying the classification.

Concerning the aim of classifications, Pettijohn (1948) writes:

> No classification independent of rock genesis can be worthy of consideration. Genesis is the ultimate aim of any study of rocks, and no descriptive classification—so-called—can be worth much unless the characters used for the classification are meaningful and significant. The only test for significance is whether they are or are not basic to the understanding of origin.

It would seem proper, therefore, to judge the current classifications on the extent to which they are truly genetic.

A useful way of assessing the genetic basis of a given classification is to classify a group of arenites deposited under similar conditions, and compare the names given with concepts of genesis derived from other sources. For example, graywacke and orthoquartzite are commonly held to be characteristic of different tectonic and environmental settings. The occurrence of these two rock-types in one formation would suggest most unusual conditions or a certain arbitrariness in the classificatory scheme used. If, after several analyses, a continuous gradation were found between graywacke and orthoquartzite, the latter alternative could be asserted with confidence.

TERMINOLOGY

Arenite.—Arenite is used in the literature in two senses. The most commonly accepted is that of Pettijohn (1957, p. 16); a descriptive term for clastic

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material of sand size without genetic or mineralogical connotations. All clastic rocks composed of sand-sized fragments are arenites in this definition.

Gilbert (1955, p. 289) proposed limiting the term "arenite" to a group of sand-sized sediments which contain less than 10 percent detrital argillaceous material. Gilbert considers "arenites" to be genetically distinct from 'wackes' which contain more than 10 percent detrital argillaceous material.

In the proposed expansion of Packham's classification which follows, the term 'arenite' is used in the broader, non-genetic, sense of Pettijohn. This usage is followed throughout the paper, except when discussing Gilbert's "arenites". In such cases the change in sense is apparent from the context.

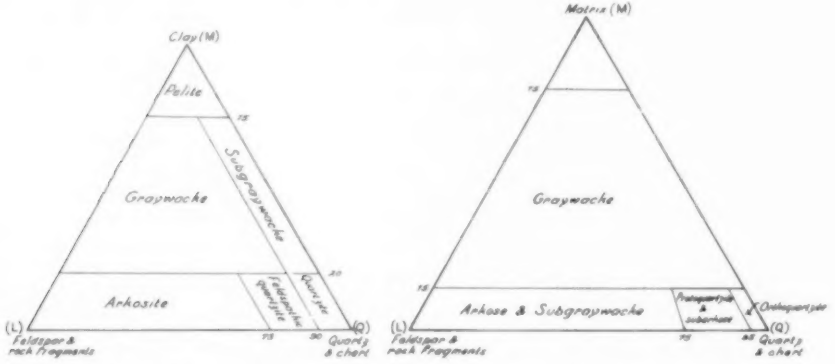
MLQ and QFR diagrams.—Two types of triangular diagrams have been widely employed in the classification of arenites. Pettijohn (1949) and Packham (1954) have used MLQ diagrams which have as parameters percentages (on a cement-free basis) of matrix (M), labiles (feldspar, rock fragments, ferromagnesians, chlorite) (L), and quartz plus chert (Q).

Gilbert (1955) on the other hand, utilized QFR diagrams, whose parameters are percentages (on a matrix- and cement-free basis) of quartz plus chert (Q), feldspar (F), and rock fragments plus other labiles (R).

Detrital carbonate is excluded from both types of diagram. Arenites containing abundant detrital carbonate require other treatment.

DISCUSSION OF CLASSIFICATIONS

Pettijohn's 1954 classification.—Pettijohn (1954) recognized three factors to be of greatest genetic significance: a maturity factor (ratio of quartz plus chert to labiles on a matrix-free basis); a provenance factor (ratio of feldspar to rock fragments), which he considers to be a measure of the plutonic and supracrustal rocks exposed in the source area; and a fluidity factor (ratio of sand detritus to martix), which gives an indication of the viscosity of the depositing medium. His classification, which is shown in the form of an MLQ



A. Pettijohn's MLQ diagram for arenites - 1949.

B. MLQ diagram for arenites derived from Pettijohn's later classification - 1954.

Fig. 1. Comparison between Pettijohn's 1949 and 1954 classifications.

diagram in figure 1B, is based on these factors. A noteworthy feature is the location of the graywacke field boundary at a 15 percent level of matrix.

Criticisms.—First, as originally defined, Pettijohn's provenance factor measures the nature of the source area only in the special case where all feldspar is plutonic and all rock fragments are supracrustal. If this factor is applied to the Miocene graywackes of the Aure Trough, Papua, described by Edwards (1950), for example, it leads to completely erroneous conclusions, for these rocks are dominantly of andesitic derivation. This difficulty seems to have been realized subsequently by Pettijohn (1957, p. 290), as his phraseology is somewhat modified.

Second, the choice of the boundary of the graywacke field, while not without reason, is arbitrary. The arenites of the Burralow Formation, Triassic, of New South Wales (Crook, 1957, p. 69), for example, belong to a formation that was deposited under broadly similar conditions, but they lie over the graywacke, protoquartzite and orthoquartzite fields of Pettijohn's diagram.

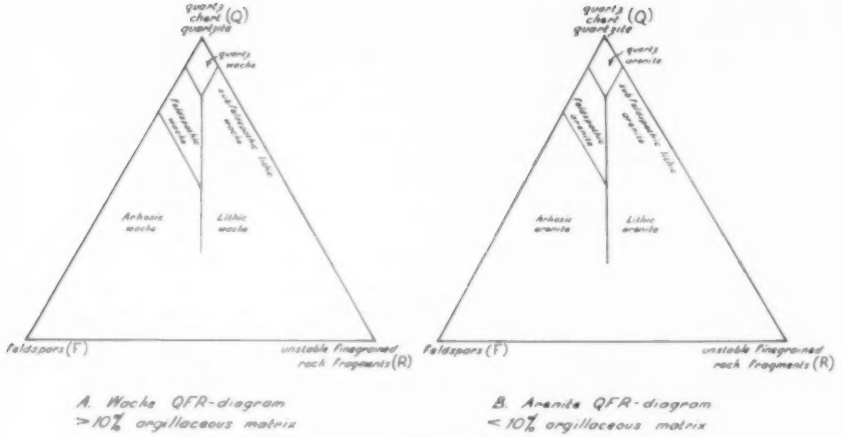
Packham (1954, fig. 1) has plotted the frequency of matrix percentages for arenites deposited from traction and turbidity currents. An overlap is shown between 8 and 32 percent of matrix, so that Pettijohn's decision to characterize graywackes by a minimum level of 15 percent matrix must be recognized as a good first approximation, but nonetheless arbitrary. Its use destroys the truly genetic nature of the classification, since the occurrence of cases such as the Triassic example cited is inevitable. This point has been well made by Folk (1954, p. 353), in discussing the confusion between texture and composition in certain classifications: " . . . one's terminology would fluctuate back and forth . . . merely at the whim of the depositional agent."

A final criticism lies in the changed definition of 'subgraywacke' from the 1949 to the 1954 classifications (see figs. 1A and 1B). This change, while bringing the term more into line with Continental usage, has added to the confusion in nomenclature.

Gilbert's classification.—Gilbert's classification is basically similar to Pettijohn's 1954 classification; it employs the same three factors, by implication, but uses two diagrams of the QFR type. The first (fig. 2A) is the 'wacke diagram' for arenites with more than 10 percent detrital matrix. Thus it is the equivalent of those parts of Pettijohn's 1954 MLQ diagram (see fig. 1B) which lie above the 10 percent level of matrix. The second QFR diagram (fig. 2B) is the 'arenite diagram', for arenites with less than 10 percent detrital matrix. It is the equivalent of the remainder of figure 1B.

Criticisms.—Gilbert's classification can be criticized in one aspect on the same grounds as Pettijohn's 1954 classification. The choice between the two diagrams depends on the arbitrary level of 10 percent matrix. Like the 15 percent level of Pettijohn it fails, and for the same reasons.

A further criticism lies in Gilbert's usage of the term 'arenite'. It is most unfortunate that this term, previously without mineralogical or genetic connotations, should have been so restricted, as it destroys the only existing satisfactory term for the general description of sand-sized sediments. Pettijohn (1957, p. 17) has already commented on the inadequacy of the term 'sandstone' for such general descriptions.



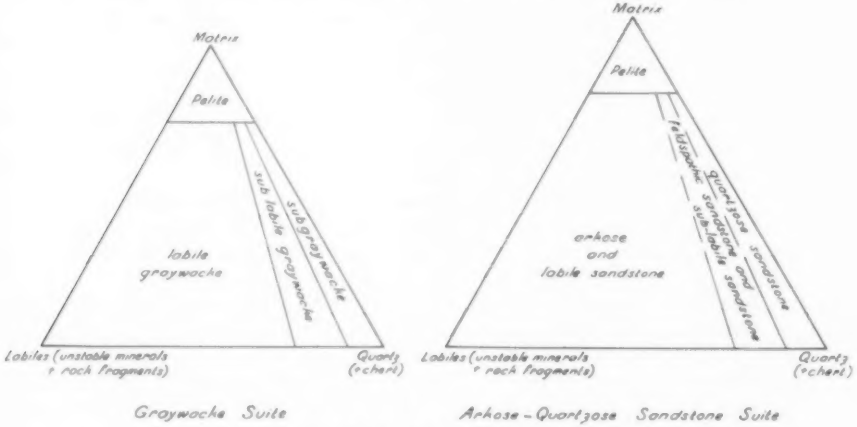
A. Wacke QFR-diagram >10% orgillaceous matrix

B. Arenite QFR-diagram <10% orgillaceous matrix

Fig. 2. QFR diagrams of Gilbert's classification (1954).

Packham's classification.—Packham (1954) utilizes, by implication, two of Pettijohn's factors: the fluidity factor and maturity factor. A new parameter is introduced, however, sedimentary structures (Packham, 1954, table 1). On the basis of sedimentary structures arenites are assigned to one of two groups, the 'graywacke suite' and the 'arkose-quartzose sandstone suite'. Each group has its own MLQ diagram on which arenites may be plotted in the normal manner. The name so derived will be at once both descriptive and genetic.

Whether Packham's classification is truly genetic depends on the value of sedimentary structures as indicators of the type of depositing current. Data obtained by numerous workers during the last ten years strongly suggest that



Graywacke Suite *Arkose-Quartzose Sandstone Suite*

Fig. 3. MLQ diagrams for arenites on Packham's classification (1954).

sedimentary structures can be validly used in the manner Packham has suggested.

By using two MLQ diagrams, Packham has avoided the arbitrariness found in Pettijohn's and Gilbert's classifications, and it is impossible for specimens from a single genetically homogeneous formation to have names implying different geneses because of slight variations in the detrital matrix content.

Criticisms.—Packham's classification, in its present form, is usable only when data on sedimentary structures are available. No provision has been made for field and laboratory nomenclature which does not imply genesis.

The term 'sandstone' is used by Packham in two senses, broadly, as a synonym of 'arenite' as used herein, and in a restricted sense, always with a qualifying adjective, to refer to arenites deposited by traction currents, for example, 'labile sandstone', 'quartzose sandstone'. This homonymy causes difficulties if one is dealing with arenites without knowledge of their associated sedimentary structures. They cannot be descriptively named on Packham's scheme without prejudging the issue. An arenite rich in quartz, but of unknown associations, cannot be called a 'quartzose sandstone' without implying the association of certain sedimentary structures, which are however unknown.

The classification is inadequate when attempting to name arenites which contain large percentages of labile material. For rocks derived from nongranitic sources only the terms 'labile graywacke' and 'labile sandstone' are available.

Folk's Classification.—Folk's classification does not utilize either QFR or MLQ diagrams, but uses a ternary diagram having quartz plus chert; feldspar plus all igneous rock fragments; and mica plus metamorphic rock fragments plus metaquartzite as parameters. The diagram is subdivided in the manner shown in figure 4. Unlike the classifications already discussed, Folk's scheme does not utilize matrix-content as a parameter, and the names given to arenites in his scheme are thus uninfluenced by the matrix-content of the rock. Al-

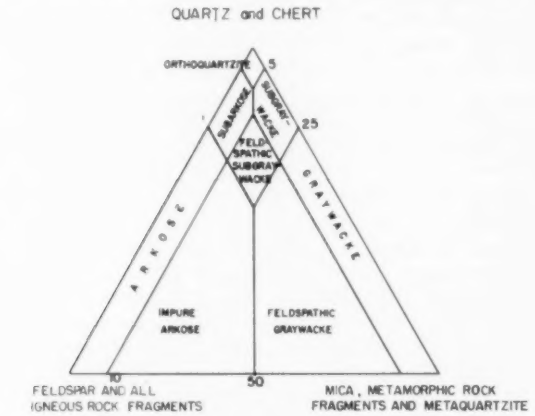


Fig. 4. Triangular diagram for Folk's classification (1954).

though matrix-content effects the plotting of arenites on MLQ diagrams in Packham's scheme (see fig. 3), the end result is the same, for variation in matrix-content does not result in changes in arenite nomenclature.

Folk's scheme does not attempt to convey information concerning mode of sedimentation, the parameters being chosen with the intent to classify arenites according to provenance. The three parameters given above are held to measure (a) detritus of sedimentary origin, or detritus which has undergone a prolonged period of chemical and/or physical modification; (b) detritus of igneous origin; and (c) detritus of metamorphic origin.

Criticisms.—The most important criticisms of Folk's classification find their source in his choice of parameters. The quartz plus chert parameter is not a completely satisfactory measure of detritus of sedimentary origin, because it may incorporate an unknown quantity of first cycle plutonic or volcanic quartz, and volcanic "chert", which may not have undergone prolonged chemical or physical weathering. Furthermore sedimentary rock fragments find no place in his parameters, and their insertion poses great difficulties.

The grouping of all igneous detritus into one parameter is unfortunate, for the mineralogical and tectonic significance of plutonic as against volcanic components in a sediment is considerable, and they should be separated in arriving at a rock name.

The lack of emphasis on mode of sedimentation is, in the author's opinion, a fundamental weakness of the scheme. It leaves no possibility of distinguishing an arenite deposited by a turbidity current in deep water from one deposited by fluvial agencies on land in those cases, which are not uncommon, where both have a large igneous component.

The extent of the difficulties raised by the choice of parameters and lack of emphasis on mode of sedimentation may be seen by comparing arenites derived from (a) an andesitic island arc; (b) a granite mass of low relief being covered by a transgressive sea; and (c) a complex orogenic belt with prominent exposures of volcanics. It is not unlikely that the arenites derived from each source will fall in the "arkose" field on Folk's diagram (fig. 4). Although this contingency can be met by the use of suitable qualifiers as Folk has suggested (1954, p. 357), it is rather unwieldy and confusing.

EXPANSION OF PACKHAM'S CLASSIFICATION

From the foregoing Packham's classification seems to be the only existing one soundly based, genetically speaking. It is proposed to use this classification as a basis for an expanded classification which will not be subject to the criticisms mentioned above.

To meet the difficulties encountered in dealing with arenites when data on sedimentary structures are not available, the author proposes a non-genetic 'arenite MLQ diagram'. This diagram (fig. 5) employs the same parameters as the graywacke and arkose-quartzose sandstone suite diagrams of Packham, and is subdivided in the same manner on the basis of the maturity factor, into 'labile arenite', 'sublabile arenite', and 'quartzose arenite'. The relationship between this new diagram and those of Packham is shown in figure 6. Arenites of unknown associations, provided they are not rich in detrital carbonate, can

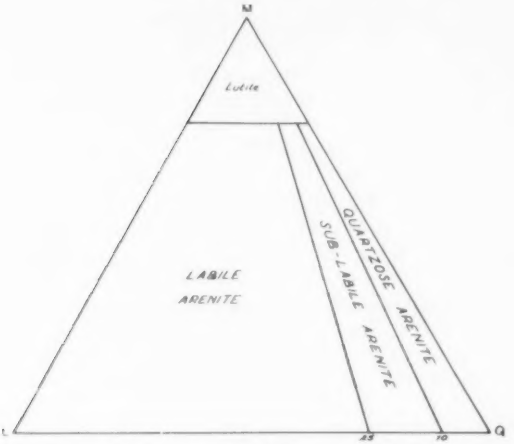


Fig. 5. Generalized MLQ diagram for arenites.

be named by reference to this diagram, and the names derived will be descriptive and non-genetic.

'Sandstone', will be restricted to sediments of inferred traction-current origin, and 'arenite' used as the generalized non-genetic term for sand-sized clastic material. This avoids the homonymy in Packham's usage and his 'arkose-quartzose sandstone suite' can then be termed simply the 'sandstone suite'.

Amplification of the terms descriptive of labile rock-types is desirable, particularly to enable distinction between labile arenites rich in feldspar and those rich in rock fragments. This can be effected by using a QFR diagram with suitable subdivisions. For simplicity only one, generalized, QFR diagram is proposed, which gives a series of names for arenites of various compositions: congruent 'graywacke' and 'sandstone' QFR diagrams may be used if data on sedimentary structures are available.

The QFR diagram proposed (fig. 7) is subdivided congruently with the arenite-MLQ diagram (fig. 6) into quartzose arenite and sublabile arenite at levels of 90 and 75 percent quartz, respectively. The sublabile arenite field is subdivided as discussed below.

The field containing rocks with less than 75 percent quartz is subdivided on the basis of ratio of feldspar to rock fragments + other labiles (the FR ratio), this ratio being calculated on a quartz-free basis. The subdivided fields are designated as follows, and have the following range of values for the FR ratio:

feldspathic arenite	FR—∞ to 3	feldspathic
lithofeldspathic arenite	FR—3 to 1	labile arenites
feldspatholithic arenite	FR—1 to 1/3	lithic
lithic arenite	FR—1/3 to 0	labile arenites

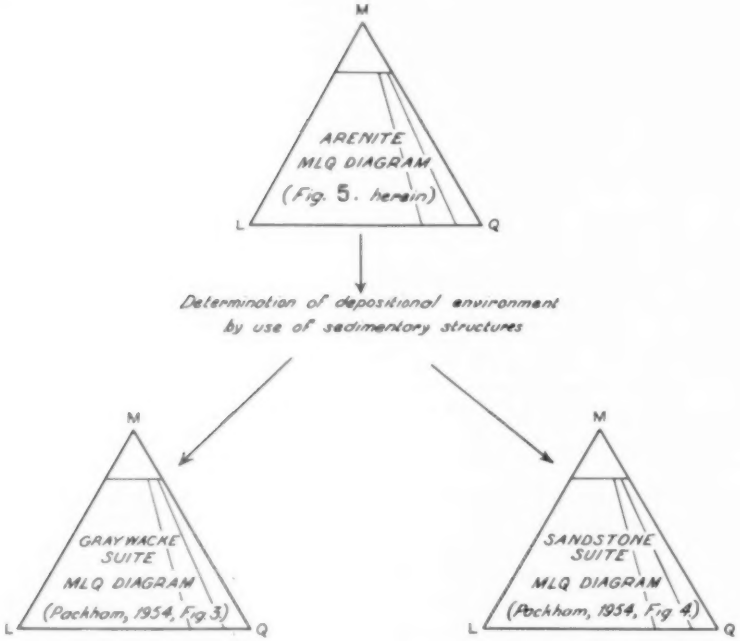


Fig. 6. Diagram showing relationship between arenite MLQ diagram proposed herein, and those of Packham (1954).

Fig. 7. Generalized QFR diagram for arenites.

The author has followed Pettijohn (1954) in using the term 'lithic' to designate arenites with abundant rock fragments.

Labile arenites rich in feldspar should logically be termed 'feldspathic arenites'. Unfortunately the adjective 'feldspathic' has been commonly applied to certain kinds of sublabile arenites. Packham (1954, p. 475) describes the sublabile equivalent of an arkose as 'feldspathic sandstone'. Gilbert (1955) uses the terms 'feldspathic arenite' and 'feldspathic wacke' for rocks which would mostly plot in the 'sublabile arenite' field of figure 6.

It is here proposed that the term 'feldspathic arenite' be reserved for labile arenites with less than 75 percent quartz and an FR ratio exceeding 3 (see fig. 7). The genetically flavored congruent terms, 'feldspathic sandstone' and 'feldspathic graywacke', should be reserved for arenites of this composition which are members of the sandstone and graywacke suites, respectively. Each of these three feldspathic rock-types includes, as derivatives of granitic terrains, the varieties 'arkosic arenite', 'arkose', and 'arkosic graywacke' respectively.

The use of the terms 'feldspathic arenite, sandstone or wacke' as descriptive of any variety of sublabile arenite should be discontinued. Pettijohn, realizing the desirability of this, has coined the term 'subarkose' which is roughly synonymous with his 1949 'feldspathic quartzite' (see figs. 1A and 1B). The genetic connotation of 'arkose' limits the value of this term, and it should be restricted to sublabile derivatives of granitic terrains, deposited by traction currents.

To overcome this difficulty it is proposed that two broad classes of sublabile arenite be recognized, 'feldspathic sublabile arenite' and 'lithic sublabile arenite', having FR ratios exceeding and less than 1, respectively (see fig. 7). As before, the term 'arenite' can be replaced by 'sandstone' or 'graywacke' when data on depositional environment are available. Subarkose then becomes a variety of feldspathic sublabile sandstone, and is, in this usage, synonymous with Packham's 'feldspathic sandstone'.

CONCLUSION

So many classificatory schemes for arenites have been proposed in recent years that it seems necessary to justify a further increase in their number. The following arguments are cited in defense of the scheme presented here:

a. It is not basically a *new* classification, but an expansion of an existing classification which removes certain shortcomings present in that classification. It should therefore be used in conjunction with this existing classification of Packham (1954).

b. Taken in conjunction with Packham's classification the present scheme enables the naming of an arenite in the field, in the laboratory, and, after examination of evidence from sedimentary structures, the assigning of a final name with both descriptive and genetic connotations.

It should be noted that the scheme proposed herein does not attempt to assign names to all kinds of arenites. This must await further work. Cases which are not covered are, for example, pyroclastic arenites, glacial arenites, and arenites with abundant detrital carbonate.

ACKNOWLEDGMENTS

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EVIDENCE FOR AN ABRUPT CHANGE IN CLIMATE CLOSE TO 11,000 YEARS AGO*

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ABSTRACT. Evidence from a number of geographically isolated systems suggests that the warming of world-wide climate which occurred at the close of Wisconsin glacial times was extremely abrupt. Surface ocean temperatures in the Atlantic Ocean increased by several degrees centigrade and deep-sea sedimentation rates sharply decreased in the equatorial Atlantic. The bottom waters of the Cariaco Trench, a restricted basin in the Caribbean, abruptly stagnated. The pluvial lakes in the Great Basin rapidly shrank from their maximum volume to nearly their present size. Silty clay which was flushed into the Gulf of Mexico during the glacial period was suddenly retained in the alluvial valley and delta of the Mississippi River and the glacially-dammed Great Lakes drainage was returned to the northern outlet. As indicated by pollen profiles a pronounced warm period in northwestern Europe also occurred at this time. In each case the radiocarbon age determinations suggest that the changes occurred in less than 1000 years close to 11,000 years ago.

INTRODUCTION

The problem of reconstructing the variations in climate which characterize the Pleistocene has long challenged the geologist. Although the collection, correlation and interpretation of data has progressed steadily during the past 100 years, the recent development of geochemical methods for both time and temperature measurement have greatly accelerated the progress in this field. The C^{14} method of age determination in particular has provided not only absolute estimates of time over the past 40,000 years but has also allowed precise correlations to be made between events in widely separated geographic areas and in vastly different depositional environments.

This paper summarizes the evidence for an abrupt world-wide change in climate close to 11,000 years ago marking the end of the Wisconsin glacial period. That this climatic change occurred suddenly was first recognized by Ewing as a result of the study of deep-sea cores (Ewing and Donn, 1956). Subsequently radiocarbon measurements on these cores were presented by Ericson, et al. (1956). The study has since been extended to other climate-controlled systems.

The evidence to be summarized is largely correlated on the basis of radiocarbon measurements. These include not only those reported in "Lamont Natural Radiocarbon Measurements" (Broecker, et al., 1956, and Broecker and Kulp, 1957) but also the results published by other laboratories. Since the period of interest spans less than 2000 years, careful attention must be given not only to the laboratory errors, which range between 100 and 500 years, but also to the possibility of systematic errors for samples of different material types and growth environments. An attempt will be made to evaluate these factors as the discussion proceeds.

The systems studied include deep-sea sediments from the Atlantic Ocean and adjacent seas, deposits from the pluvial lake area of the western U. S. A., sediments from the Great Lakes and their associated drainage networks and

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the pollen sequences of northwestern Europe. Each of these systems shows a strong dependence on climate.

EVIDENCE FROM DEEP-SEA SEDIMENTS

Surface temperatures.—The first and most important of these systems is the ocean. Its vast extent and fairly rapid internal mixing rate enable it to record world-wide climate changes, being less influenced by local events than any other system. This broad picture is recorded in a number of different ways. Three of these have been investigated in the course of this study: 1) variations in surface ocean temperature, 2) changes in the rate of deep-sea sedimentation, 3) stagnation of restricted basins.

A record of surface ocean temperature is provided by the tests of planktonic foraminifera which make up the majority of the coarse fraction ($>74\mu$) of the carbonate material in globigerina ooze. This record can be read by either the micropaleontological method used by Ericson and Wollin (1956) or the oxygen-isotope method used by Emiliani (1955). The first method is based on the temperature dependence of the relative abundance of certain species of planktonic foraminifera (Schott, 1935). By observation of the relative abundance of these species an estimate of the relative surface water temperature for the time corresponding to any depth in the core can be made. The second method relies on the temperature dependence of the oxygen-isotope fractionation that occurs during the formation of carbonate. The isotopic composition of the oxygen from carbonate samples can be measured with a precision equivalent to 1°C (Urey, 1951). The uncertainty in the absolute temperature computed from these ratios is somewhat larger than 1°C because the oxygen-isotope ratio for the sea water from which the carbonate was precipitated must be estimated from other considerations. For example, Emiliani (1955) has pointed out that the preferential storage of O^{16} in glacial ice could have caused a significant change in the ratio for seawater during Wisconsin time (equivalent to at least 2°C change in temperature).

As shown in figure 1 the two methods have shown excellent agreement where they have both been applied to the same core. Both methods show a rather sharp increase from the relatively cool temperatures of Wisconsin time to the warm temperatures of the present. The magnitude of this change as given by the paleotemperature method is 6° to 10°C (Emiliani, 1955), depending on the assumptions made about the glacial storage effect.

Since the span of time required for the temperature change is critical to the arguments which follow, it is important to consider what processes might alter the true shape of the curve. The curve might conceivably be sharpened by erosion or removal by slumping. Such effects should be apparent as sudden changes in lithology or as time discontinuities. Careful inspection has not revealed either of these effects associated with the temperature transition in the cores of interest. On the other hand, as pointed out by Emiliani (1957), post-depositional mixing of the sediment by bottom organisms would tend to spread out the change. Such activity is known to occur but is difficult to evaluate quantitatively. It may be concluded that the temperature transition is at least

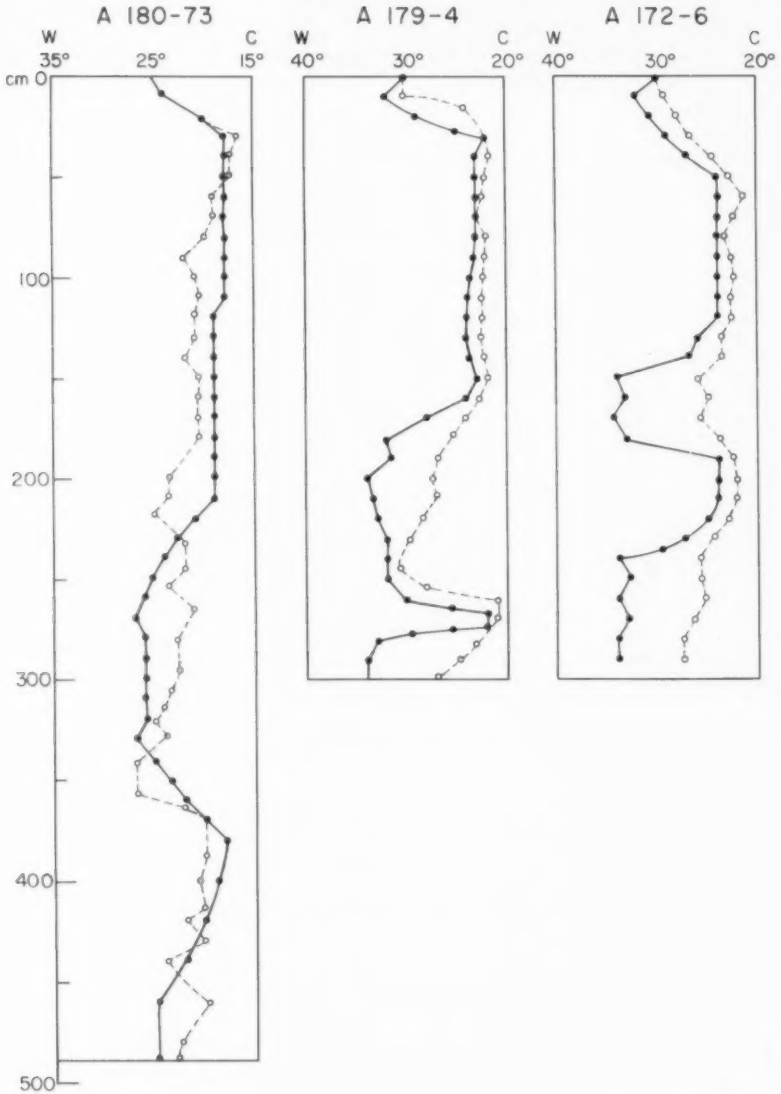


Fig. 1. Comparison of surface ocean temperature curves based on foraminifera abundance (Ericson and Wollin, 1956a and 1956b; solid curves, warm-cold scale) with those based on oxygen isotope measurements (Emiliani, 1955; dotted curves, degrees centigrade scale).

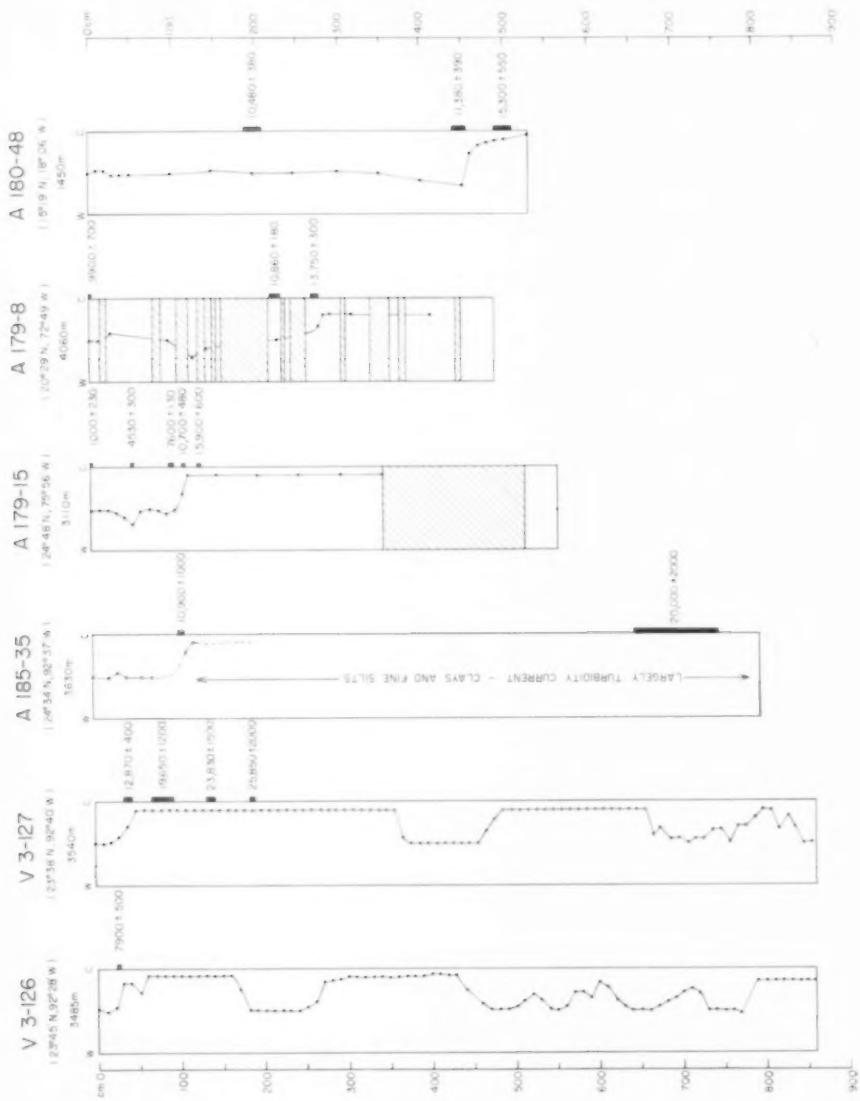
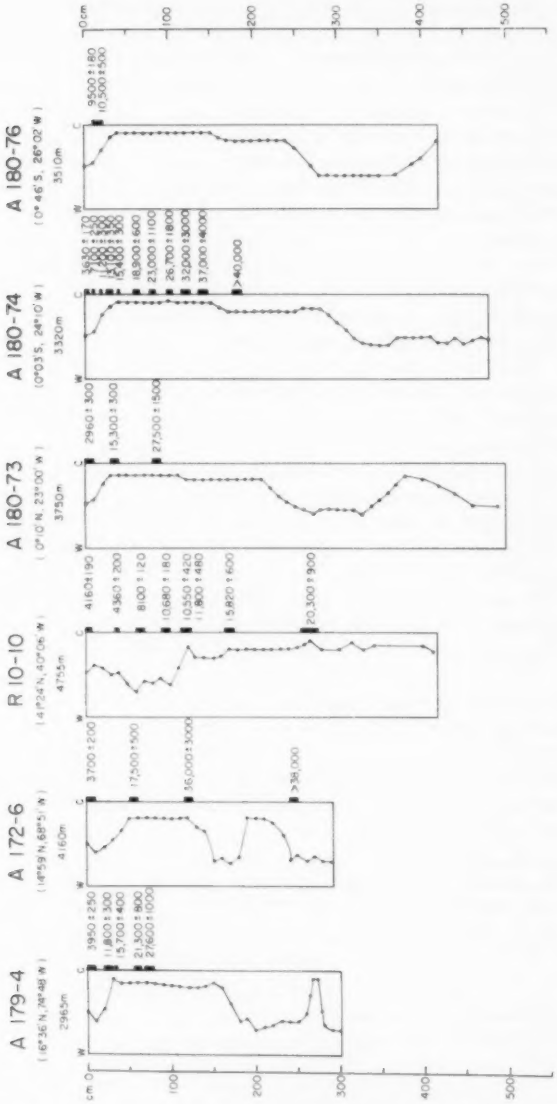


Fig. 2. Foraminifera temperature curves and radiocarbon ages for deep sea cores. The climate curves were constructed by Ericson (Ericson and Wollin, 1956a and b; Ewing,



et al., 1958). The radiocarbon ages on cores A 179-4, A 172-6 and A 180-73 were obtained by Rubin and Suess (1955 and 1956). The dates on the other cores were obtained at the Lamont Geological Observatory (Broecker, et al., 1956; Broecker and Kulp, 1957).

as sharp as indicated by the temperature curves.[1]

Since the carbonate material in the cores of interest consists mainly of foraminiferal tests and coccoliths, both of which grow in the surface water, C^{14} age determinations can be made by comparing the C^{14}/C^{12} ratio in the core material with that in dissolved carbonate in present day surface ocean water. The difference is attributed to radioactive decay. There are two major potential sources of error in such determinations: 1) post-depositional exchange, 2) presence of reworked carbonate material. The fact that the oxygen isotope record is preserved and that C^{14} ages of $>30{,}000$ years have been observed on core materials suggest that the amount of exchange is small and should be negligible in the age range of interest. Suess (1956) pointed out that comparison of C^{14} ages on the coarse and fine fraction should give an indication as to the presence of reworked carbonate. In one case he found that the fine fraction showed an appreciably greater age. Two such comparisons by Broecker and Kulp (1957) showed a greater age for the fine fraction in one case but no significant difference in the other. For the age range of interest reworked carbonate appears to be the only important source of systematic error.[2] Thus it may be concluded that the ages obtained are either equal to or *greater than* the true age of the core material.

The micropaleontologic temperature curves obtained by Ericson and Wollin (1956) and the radiocarbon dates obtained by Rubin and Suess (1955, 1956), Broecker, et al. (1956), Broecker and Kulp (1957) are shown in figure 2. With the exception of cores A 179-8 and A 185-35, which contain numerous turbidity current deposits and core A 180-48 which shows an abnormally high sedimentation rate, the cores may be taken to represent normal deep-sea sedimentation. A more complete discussion of the lithology of these cores has been published elsewhere (Ericson, et al., 1956; Ericson and Wollin, 1956a, and 1956b; Ewing, et al., 1958).

Table 1 summarizes the data. The best estimate of the age of the midpoint of the temperature transition in each core is given in column 7. Columns 5 and 6 give respectively the estimates for the maximum age for the beginning of the temperature transition and the minimum age for the end. The difference between these two ages provides an upper limit on the duration of the transition interval (column 8).

[1] Emiliani (1957) concludes that the temperature changes shown in several of the cores used in this study (R 10-10, A 180-48, A 179-15) are anomalously sharp and that the more gradual changes suggested by some of the cores (A 172-6, A 180-73, A 180-74) give a better picture of the actual shape of the temperature transition. Since the latter are slow deposition cores mixing by bottom borers would be more effective in spreading out the time record. Unless erosion removed a portion of the rapid deposition cores at precisely the time when the temperature was changing it is difficult to postulate a mechanism for sharpening the curves. Neither the lithologic or age data gives any indication of loss of the transition period sediment by erosion. For these reasons more weight is given to the cores showing sharp transitions.

[2] Emiliani (1957) has suggested that mixing by bottom borers can make the age at a given depth in a core too old. As evidence he uses the finite ages of the tops of several cores. However, if the mixing process has proceeded at a more or less constant rate, the amount of younger material mixed downward should roughly compensate for the amount of older material mixed upward in samples collected from below the depth of mixing. In this case ages at the depths of the temperature break should be unaffected by mixing. Also, the existence of rather sharp color changes in many of the equatorial cores suggests that the mixing produced by bottom borers is more limited than Emiliani suggests.

The majority of the midpoint ages lie close to 11,000 years. Those which are significantly older probably reflect the influence of reworked carbonate. Although the midpoint ages close to 11,000 years may also be somewhat too old, the excellent agreement between cores of widely different lithology and geographic locations suggests that this effect is small (<1000 years).

The maximum time for the transition is in all cases less than 6000 years. Since the manner in which the limits were determined, the finite spacing of the temperature measurements, and the possibility of homogenization by bottom borers all tend to increase the magnitude of this range, the smaller times ($\sim$2000 years) obtained for cores R 10-10 and A 180-48 and the very small time ($\sim$200 years) for V 12-97 are probably significant.[3] No minimum estimate can be made from the data in hand.

The conclusion is drawn that a large portion of the Atlantic Ocean underwent a temperature increase of 6° to 10°C during a period of less than 2000 years and that the midpoint of this change was within 300 years of 11,000 years ago.

Sedimentation rate.—A study of the variation in sedimentation rate with time in core A 180-74 from the mid-equatorial Atlantic by Broecker, et al. (1958) indicates that both the carbonate and the clay fraction in this core underwent a significant decrease in sedimentation rate close to 11,000 years ago. Cumulative plots of weight of clay and of weight of carbonate as a function of time before present as determined by radiocarbon dates (Broecker, et al., 1956; Broecker and Kulp, 1957) is shown in figure 3. From the change in slope close to 11,000 years ago it can be shown that the clay rate decreased by a factor of 3.7 and the carbonate rate by a factor of 2.1. Although this represents only one locality and does not permit an extrapolation to other parts of the Atlantic, the data supports the hypothesis that an abrupt change in climate occurred close to 11,000 years ago.

Ventilation of restricted basins.—The depletion of oxygen from the bottom water in restricted marine basins is often recorded in the sediments by the preservation of organic materials, the extermination of the benthic fauna, and the presence of H_2S gas. Such a situation exists in the upper 5 to 10 meters of sediments in the Cariaco Trench off Venezuela. Although the stagnation of the deep water in the trench appears to have been continuous during the period of deposition of this sediment, the presence of a layer of oxidized clay beneath the organic rich ooze demonstrates aeration at some time in the past. A radiocarbon date on organic material from the base of the anaerobic layer indicates that the abrupt stagnation of the trench occurred within 300 years of 11,000 years ago (Heezen, et al., 1958 and 1959).

EVIDENCE FROM FRESH-WATER DEPOSITS

Deposits formed by fresh-water drainage systems also record the abrupt climatic change seen in deep-sea deposits. Two such systems will be considered:

[3] Emiliani (1957) concludes that the transition occurred gradually over a period of about 8000 years. He considers cores R 10-10 and A 179-15 which show rapid transitions unreliable because of the large changes in sedimentation rate suggested by the ages. Ericson (personal communication) who did the lithologic studies of these cores, considers them both reliable in the depth range of interest. Core A 179-15 shows no evidence of abnormal sedimentation above a depth of 300 cm. Even if abnormalities were present it is difficult to construct a sequence of events which would yield the observed temperature curves and radiocarbon dates if a gradual temperature change over a period of 8000 years did occur.

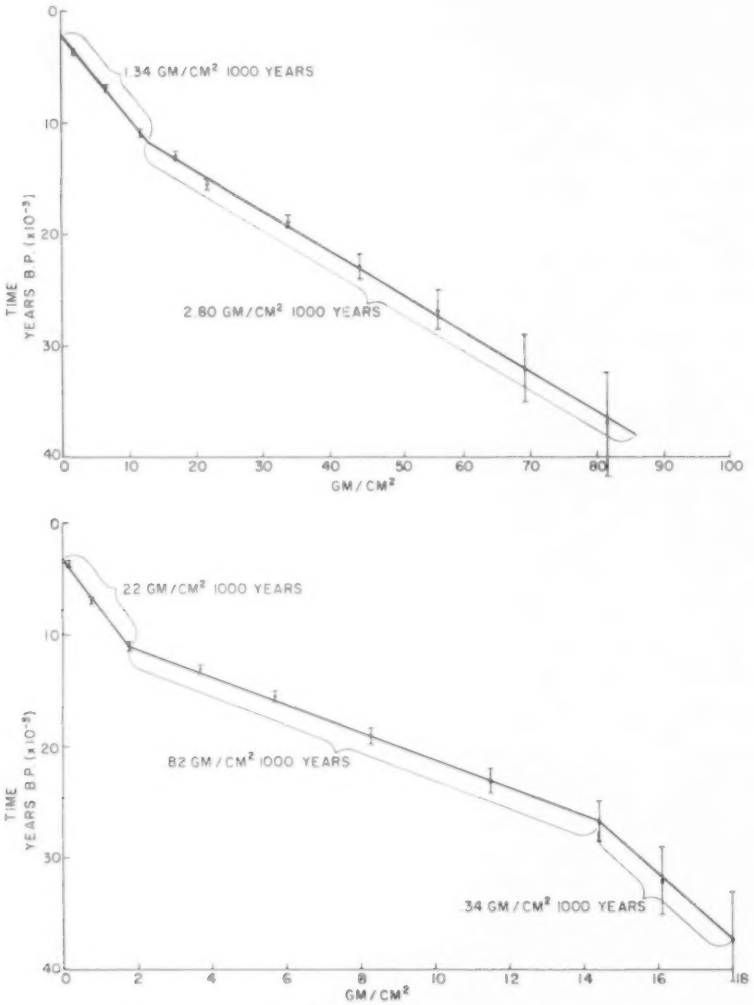


Fig. 3. Cumulative weight of $CaCO_3$ (upper diagram) and of clay (lower diagram) as a function of time in the past (Broecker, et al., 1958). The points represent radiocarbon ages with their respective errors. The slope of the lines connecting points gives the sedimentation rate at a given time. For both components a sharp change in rate occurs close to 11,000 years ago.

1) the system of lakes in the Great Basin of the western United States and 2) the main midcontinent drainage system consisting of the Great Lakes, the Mississippi River and the St. Lawrence River.

Pluvial lakes.—The Great Basin lakes are of particular interest since they are direct indicators of climate. Since these lakes have no outlet, their size is controlled primarily by a combination of rainfall and evaporation rates. As shown by Broecker and Orr (1958) the lakes respond rapidly to climatic change so that their level at a given time provides an excellent index of climate. Radiocarbon dates for Searles Lake by Libby (1955) (see Flint and Gale, 1958) and for lakes Lahontan and Bonneville by Broecker and Orr (1958) provide reasonably detailed data on the level of these lakes as a function of time.

Since these curves are based primarily on C^{14} dates obtained on material formed in fresh water lakes, the problem of estimating the initial C^{14} concentration in such materials must be considered. As shown by Deevey, et al. (1954) in some cases the concentration is significantly lower than in terrestrial plants or surface ocean water. Broecker and Orr (1958) used the present C^{14}/C^{12} ratio in the dissolved carbonate of Pyramid Lake as the control value. Broecker and Walton (1959) on the basis of numerous C^{14} measurements on currently forming materials from Great Basin fresh-water systems concluded that the C^{14}/C^{12} ratio in these lakes was within 5 percent of the present Pyramid Lake value during high water periods. This corresponds to a 400-year age uncertainty.

A second possibility of systematic error, especially for carbonate samples, is the incorporation of C^{14} by the sample after deposition. This could occur through transport and redeposition by rain or ground water or by exchange with the atmosphere. Experiments by Broecker and Orr (1958) suggest that contamination by atmospheric exchange is negligible in nearly all cases. Only the dry climate of the Great Basin and the internal consistency of the data can be used as evidence against the importance of redeposition. The ages given by Broecker and Orr on carbonate materials are probably good to 400 years but in some cases may represent only minimum estimates.

The available radiocarbon data, summarized in tables 2 and 3, strongly suggest an abrupt decrease in level from near maximum to near desiccation close to 11,000 years ago. The evidence may be summarized as follows. Except for the samples from the Winnemucca Cave area, the tufa samples from the highest level of Lake Lahontan yielded ages between 11,000 and 12,000 years B.P. averaging 11,600 years B.P. Samples from the Winnemucca Cave area suggest a second maximum close to 10,000 years ago. Although the Bonneville samples show evidence of high lake levels at both of these times no distinct separation into two groups exists. The Searles Lake data indicate that the now-dry lake contained water prior to 11,000 years ago. Data from each of the three lakes clearly demonstrates the return of arid conditions close to 11,000 years ago. Searles Lake became completely desiccated. Lake Lahontan fell below the level of Fishbone Cave and Leonard Rock Shelter and Lake Bonneville fell below the level of Danger Cave and deposited a sequence of carbonates on the salt flats.

The evidence for a rapid rise following the low levels of these lakes is problematic. In both the Lahontan and the Bonneville basins C^{14} data suggest a maximum at about 10,000 years ago. No evidence for this maximum appears

to be present in the Searles Lake record, however. More work is needed to settle this question.

The events recorded in the deposits of the Great Basin lakes are summarized in figure 4. A period of continuous relatively high-water levels be-

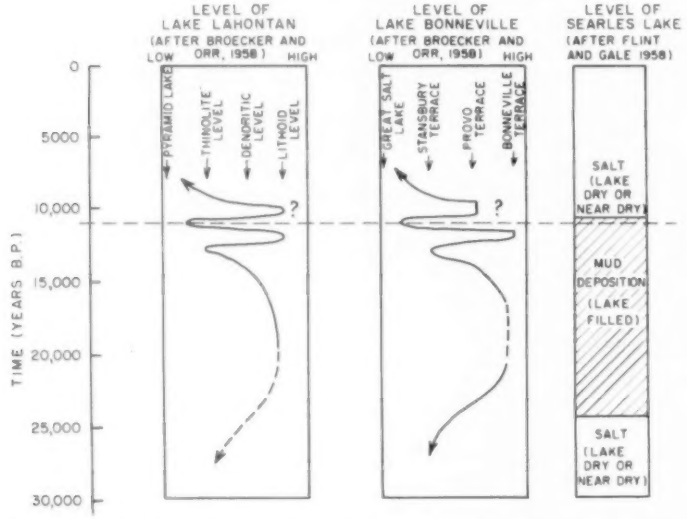


Fig. 4. The height of the major Great Basin lakes as a function of time as interpreted from radiocarbon ages.

ginning about 25,000 years was culminated by a sharp drop in lake level close to 11,000 years ago. This drop may have been followed by a brief high-water period ending about 9500 years ago. Since that time the lakes have had levels similar to those observed at present.

Midcontinent drainage system.—The midcontinent drainage system records climate in a somewhat more indirect manner. The sediments in the alluvial valley of the Mississippi River, as well as those on the Sigsbee Abyssal Plain of the Gulf of Mexico, record a marked change in the operation of the drainage system. Ewing, et al. (1958) have shown on the basis of sediment core studies that great thicknesses of gray silty clay were deposited on the abyssal plain during late Wisconsin time. They showed that this silty clay emanated from the mouth of the Mississippi River and was transported by turbidity currents. Radiocarbon dates (Broecker and Kulp, 1957) on globigerina ooze from immediately above the silty clay sequence from one of the cores (A 185-35) indicates that the supply of silty clay was cut off abruptly close to 11,000 years ago.

The evidence used by Ewing, et al. (1958) to establish the origin of the silty clay deposits is summarized in an idealized diagram in figure 5. Cores (see, for example, V 3-127, fig. 2) on knolls rising above the abyssal plain

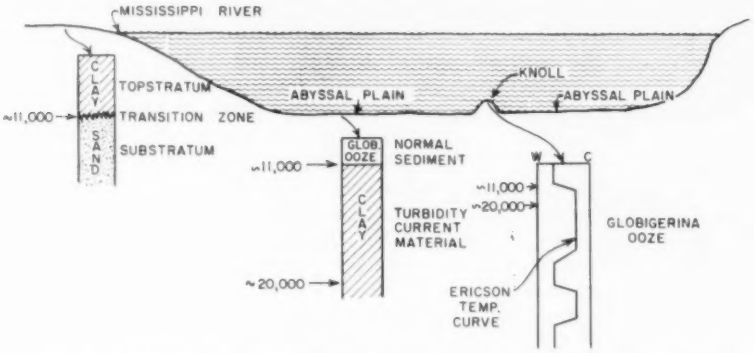


Fig. 5. Idealized diagram showing relationships of sediments on the floor of the Gulf of Mexico to those in the alluvial valley of the Mississippi River. The Gulf sediments are described by Ewing, et al. (1958) and the alluvial valley sediments by Fisk and McFarlan (1955).

are composed entirely of foraminiferal ooze, show normal climatic curves and have, as shown by radiocarbon dates, sedimentation rates similar to those in other normal deep sea oozes. Since the cores taken on the abyssal plain surrounding the knolls all show a thick silty clay sequence, Ewing, et al. conclude that the sediment must have been carried in along the bottom rather than having fallen from the surface.

Further evidence for an abrupt change in the operation of the Mississippi River system is found in the sediments on the alluvial plain in Louisiana. Fisk (1955) has classified the sediments filling the channel cut by the river during the last period of sea level lowering into two categories; the substratum consisting of sand and gravel deposits and the top stratum consisting of silt and clay. A number of radiocarbon dates (Broecker, et al., 1956; Broecker and Kulp, 1957; Brannon, et al., 1957) on samples taken near this transition zone indicate that it has an age close to 11,000 years. The results are summarized in table 4. It seems reasonable to believe that whereas much of the clay and silt load of the Mississippi River was swept beyond its channel and beyond the continental shelf into the Gulf of Mexico during the late Wisconsin, the characteristics of the river changed close to 11,000 years ago in such a manner that these clays and silts were deposited in the present alluvial valley and in the modern delta. In the absence of other evidence it is difficult to say whether this change was brought about by a change in sea level, discharge, or quantity and character of the detrital load.

The level of Lake Michigan provides an indirect index of climate. High levels are thought to correspond to times when glaciers covered the Straits of Mackinac causing the lake to drain to the south. On the other hand, when the ice receded to a position north of the glacially depressed straits drainage to the east (perhaps via the St. Lawrence) allowed the lake level to fall. Thus levels of Lake Michigan at or below its present level indicate periods of relatively warm climate.

Evidence for low water intervals in Lake Michigan close to 11,000 years ago is provided by both the Two Creeks Forest dated at 11,300 years B.P. (see table 5) and the peat bed exposed at South Haven dated at 11,200±600 (Crane, 1956), 10,860±350 (Rubin and Suess, 1955), and 10,790±200 (Preston, et al., 1955). The use of this data to support a warming in climate close to 11,000 years ago is complicated by the Valders readvance. If the age averages of 11,300 for Two Creeks and 10,900 for South Haven are accepted at face value and if the Two Creeks Forest was overrun by Valders ice shortly after growth, then two low levels for Lake Michigan, one preceding and one following the Valders, are required. The consequent high advance and retreat rates of the Valders ice can be avoided by assuming that the Two Creeks Forest and South Haven peat are both pre-Valders in age. This would require that either or both of the radiocarbon averages are slightly in error or that a significant lag occurred between the growth and destruction of the Two Creeks Forest. Again, as in the case of the Great Basin, more work is needed to resolve the multiple events which occurred in the time interval between 10,000 and 12,000 years ago.

Radiocarbon ages on marine shell from the St. Lawrence Valley provide additional evidence for a rapid ice retreat. In order for these glacially depressed lowlands to be invaded by marine waters the ice must have retreated considerably from its maximum extent (see Flint, 1956). The results are as follows: Hull, Ontario, Y 215, 10,630 ± 330, Ottawa, Ontario, Y 216, 10,850 ± 330, and Montreal, Quebec, 11,370 ± 360 years (Preston, et al., 1955). Again the weighted average lies slightly below 11,000 years.

Leverett and Taylor (1915), however, correlated the Champlain Sea with the Lake Algonquin stage of Lake Michigan and more recently Flint (1956) correlated it with the Lake Chippewa stage. In either case the Champlain Sea invasion would be a much more recent event (4000 to 5000 years B.P.). A radiocarbon date of 9430±250 on a peat sample from sediments post-dating the Champlain Sea (Terasmae, 1959) verifies the antiquity of the shell ruling out the explanation given by Flint (1956) that the shell contained considerable carbonate derived from ancient limestones.

EVIDENCE FROM POLLEN PROFILES

Another index of climate is the type of plant and animal remains found in terrestrial deposits. Of these the pollen profiles of northwestern Europe have been most thoroughly studied and are best understood. Also, a large number of radiocarbon measurements are available allowing a fairly detailed chronology to be established (see table 6). A portion of this profile is reproduced in figure 6. The outstanding feature of all the diagrams is the pronounced warm period referred to as *Alleröd*. It is preceded and followed by colder climates, the Older Dryas and Younger Dryas respectively. The available radiocarbon data are summarized in table 6. From these average ages for the various pollen zones and for the transition can be computed. These averages are shown in figure 6. It is clear that the warm *Alleröd* climates prevailed during the period of increase in surface ocean temperature. A problem exists in that there is not a unidirectional change in climate from cold to warm following the Older

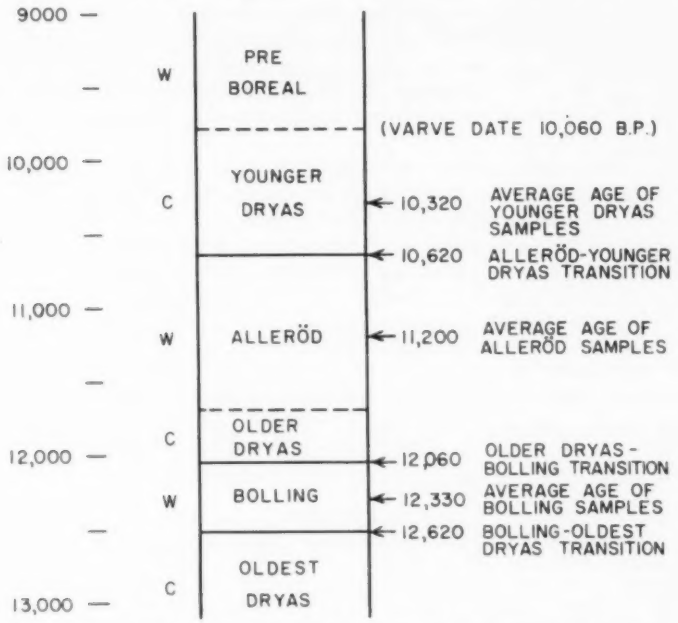


Fig. 6. Sequence of climate periods in the standard European pollen profile (based on diagram given by Barendsen, et al., 1957). The average ages for the periods and transitions are based on the data summarized in table 6. Warm periods are indicated by W and cold by C. No radiocarbon data are available for the dotted transitions.

Dryas for the cold climate is re-established during the period from approximately 10,650 to approximately 9800 years ago. The significance of this oscillation is not clear at present. It is interesting to note that an identical oscillation appears in the Great Basin and Great Lakes chronologies. It is entirely possible that the sharp change in oceanic conditions correlates with the post Younger Dryas rather than the pre Younger Dryas warm period as has been implied above.

CONCLUSIONS

From the evidence listed above it is clear that a major fluctuation in climate occurred close to 11,000 years ago. The primary observation that both surface ocean temperatures and deep sea sedimentation rates were abruptly altered at this time is supplemented by evidence from more local systems. The level of the Great Basin lakes fell from the highest terraces to a position close to that observed at present. The silt and clay load of the Mississippi River was suddenly retained in the alluvial valley and delta. A rapid ice retreat opened the northern drainage system of the Great Lakes and terrestrial temperatures rose to nearly interglacial levels in northwestern Europe. In each case the transition is the most obvious feature of the entire record.

Correlation of these systems on a finer scale is difficult in that oscillations preceding and following the major change in the case of the European pollen profiles, Great Basin lakes and Great Lakes region have not been observed in the record left in the Mississippi alluvial deposits or deep ocean deposits. More work is needed before a satisfactory explanation can be given for these differences.

Certainly if the abruptness of such a major change in world climate can be firmly established it will be of the utmost importance that acceptable theories are able to account for it. It is interesting to note that the recent "Theory of Ice Ages" proposed by Ewing and Donn (1956 and 1958) was stimulated by the observation that the change in climate which occurred at the close of the Wisconsin glacial period was extremely abrupt.

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TABLE 1

Estimate of time interval during which the increase in surface ocean water temperature occurred

1	2	3	4	5	6	7	8	9
Core	Minimum depth of end of change (cm)	Maximum depth of start of change (cm)	Depth of midpoint (cm)	Maximum age of start of change (yr)	Minimum age of end of change (yr)	Age of midpoint (yr)	Time span for change from Wisconsin to Recent temperature (yr)	Laboratory
				North Atlantic				
P 10-10	100	120	110	11,650	10,500	10,920	<1850	L
A 179-15	100	120	110	13,600	8200	10,450	<5400	L
A 179-8*	225	280	270	15,200	10,500	13,500	<4700	L
				Equatorial Atlantic				
A 180-74	10	35	18	14,600	7500	10,750	<7100	L
A 180-73	10	30	18	15,000	—	11,300	—	W
A 180-76	10	35	20	—	—	10,750	—	L
A 180-48*	450	480	457	13,500	11,600	12,100	<1900	L
				Caribbean				
A 172-6*	10	40	35	19,000	—	—	—	W
A 179-4*	15	30	24	14,200	—	11,000	—	W
				Gulf of Mexico				
A 185-35*	—	—	105	—	—	10,900	—	L
V 3-126	20	60	40	—	—	10,900	—	L
V 3-127	30	50	40	13,900	—	12,900	—	L
				Cariaco Trench				
V 12-97	445	455	450	10,950	10,750	10,850	<200	L

* Cores which might contain a substantial amount of reworked carbonate material. Ages quoted may hence be considered maximal.

W—Washington (Rubin and Suess, 1955, 1956).

L—Lamont (Broecker et al., 1956; Broecker and Kulp, 1957; Olson and Broecker, 1959).

TABLE 2

Materials from deposits formed during high water periods of the Great Basin lakes

Height Above 1890 Lake Level (feet)	Location	Material	Sample No.	Age (years)
	Pyramid Lake Basin			
525	Lake Winnemucca Cave Area, Nev.	tufa	L 289-G*	9700 ± 200
525	Lake Winnemucca Cave Area, Nev.	tufa	L 356-G*	10,000 ± 220
411	Lake Winnemucca Cave Area, Nev.	tufa	L 356-H*	9700 ± 200
560	Lake Winnemucca Cave Area, Nev.	tufa	L 364-AA*	9500 ± 200
570	Anaho Island Pyramid Lake, Nev.	tufa	L 289-N*	11,800 ± 200
520	Anaho Island Pyramid Lake, Nev.	tufa	L 289-M*	11,700 ± 200
390	Anaho Island Pyramid Lake, Nev.	tufa	L 289-L*	11,570 ± 250
560	Mullen Pass Pyramid Lake, Nev.	tufa	L 289-I*	11,250 ± 350
250	Fishbone Cave Lake Winnemucca, Nev.	tufa	L 289-C*	11,700 ± 500
570	Anaho Island Pyramid Lake, Nev.	tufa	W 442**	12,050 ± 400
	Great Salt Lake Basin			
660	South end Oquirrh Mtns., Utah	tufa	L 363-D*	11,000 ± 600
660	South end Oquirrh Mtns., Utah	tufa	L 435-G*	11,300 ± 250
660	South end Oquirrh Mtns., Utah	tufa	L 435-C*	10,600 ± 300
>660	South end Oquirrh Mtns., Utah	tufa	W 409**	11,300 ± 300
600	Pleasant View	tufa	W 456**	11,650 ± 450
	Salient, Ogden, Utah			
400	Weber River Delta Ogden, Utah	marl	W 382**	12,960 ± 350†
400	Weber River Delta Ogden, Utah	peat (from W 382)	W 326**	9925 ± 300†
400	Weber River Delta Ogden, Utah	peat (repeat W 326)	W 440**	10,260 ± 300†
	Searles Lake Basin			
—	Searles dry lake, California	organic material from top of lake muds	C 894***	10,494 ± 560
—	Searles dry lake, California	carbonate from top of lake muds	Y 574-a****	11,810 ± 140
—	Searles dry lake, California	organic material from top of lake muds	Y 574-b****	10,700 ± 130

* Broecker and Orr (1958)
** Rubin and Alexander (1958)
*** Libby (1955)
**** Flint and Gale (1958)

† A new set of samples collected from this locality by one of the authors (Wallace S. Broecker) yielded ages of 9500 ± 200 for the organic fraction and 9700 ± 200 for the carbonate fraction. The high age obtained by the Washington laboratory for the original marl has been checked and confirmed (Rubin, personal communication) strongly suggesting that this sample contained reworked detrital carbonate. Since these peats are overlain by lake sediments, these dates provide excellent evidence for a post 11,000 year B.P. high lake stand.

TABLE 3

Materials from deposits formed during low water periods of the Great Basin lakes

Height Above 1890 Lake Level (feet)	Location	Material	Sample No.	Age (years)
		Pyramid Lake Basin		
180	Fishbone Cave Lake Winnemucca, Nev.	twigs overlying lake sediments	L 245*	11,200 ± 250
—	Leonard Rock Shelter Humboldt Lake, Nev.	guano overlying lake sediments	C 599**	11,200 ± 570
90	Needles Area Pyramid Lake, Nev.	outermost tufa layer on dome	L 364-CE*	8500 ± 200
		Great Salt Lake Basin		
50	Danger Cave, Bonneville Salt Flats, Utah	sheep dung overlying beach gravels	M 118****	11,000 ± 700
50	Danger Cave, Bonneville Salt Flats, Utah	wood overlying lake deposits	C 610**	11,150 ± 570
50	Danger Cave, Bonneville Salt Flats, Utah	twigs associated with M 118	M 119****	10,400 ± 700
35	Hooper, Utah	plant stems in growth position	W 386***	9730 ± 350
17	Bonneville Salt Flats Knolls, Utah	carbonate from one foot beneath surface	L 485*	11,150 ± 450
		Searles Lake Basin		
—	Searles dry lake California	organic material from mud within upper salt	RC-36*****	10,270 ± 450
—	Searles dry lake California	organic material from mud within	RC-50*****	11,400 ± 600
—	Searles dry lake California	upper salt carbonate from RC-50	RC-50c*****	9900 ± 500
—	Searles dry lake California	trona from base of upper salt	W-248***	8550 ± 250

* Broecker and Orr (1958)

** Libby (1955)

*** Rubin and Alexander (1958)

**** Crane (1956)

***** Flint and Gale (1958)

TABLE 4

Radiocarbon dates defining the transition from sand to clay deposition in the Mississippi Alluvial Valley

Location	Sample Depth (feet)	Depth to Transition Zone (feet)	Sample No.	Age (years)
La Fourche Parish, La.	95	150	HOR-73***	8800±180
Duck Lake Area, La.	125	140	L-175B*	9750±550
Dulac Area, La.	150	210	L-291X**	10,700±150
Grand Isle Area, La.	215	245	L-291G**	11,050±300
Grand Isle Area, La.	240	245	L-291H**	10,530±350
Bayou Pigeon Area, La.	220	160	HOR-126***	13,650±300

* Broecker, et al., 1956
** Broecker and Kulp, 1957
*** Brannon, et al., 1957

TABLE 5

Radiocarbon dates on Two Creeks forest samples

Laboratory	No. of Samples	Average Age (years)
Chicago	4	11,400±350 (Libby, 1955)
Yale	1	11,130±350 (Preston et al., 1955)
Washington	2	11,375±150 (Suess, 1954)
Michigan	1	10,550±450 (Crane, 1956)
Weighted Average		11,300±130

TABLE 6

Radiocarbon dates for northeastern Europe pollen profiles

	Sample No.	Age (years)
Younger Dryas		
	GRO 419	10,345±275
	K 111	10,300±350
	Y 139-3	11,350±150*
Younger Dryas/Alleröd Boundary		
	K 101	10,890±240
	GRO 454	10,995±250
	W 82	10,260±200
	W 86	10,510±180
	K 102	10,500±400
	Y 157A	10,560±200
	H 105-87	11,500±300*

TABLE 6 (Continued)

Alleröd		
	K 103	11,060 ± 480
	K 113	10,930 ± 380
	K 104	10,990 ± 240
	K 110	10,770 ± 360
	K 105	11,800 ± 410
	K 106	11,880 ± 340
	K 112	11,700 ± 360
	K 107	11,160 ± 320
	C 337	11,044 ± 500
	GRO 909	11,025 ± 120
	GRO 907-937	10,650 ± 120
	GRO 920	10,660 ± 90
	GRO 647	11,230 ± 400
	GRO 925	11,065 ± 120
	GRO 948-933	11,700 ± 90
	GRO 947	11,470 ± 90
	GRO 921	11,560 ± 100
	GRO 410	11,200 ± 320
	GRO 413	11,560 ± 260
	H 1-8	11,900 ± 500
	H 1-48	11,800 ± 300
	H 21-18	11,550 ± 280
	H 18-11	11,930 ± 290
	H 75-68	11,450 ± 180
	Y 139-1	12,500 ± 180*
	Y 139-2	10,880 ± 160
	Y 442	11,220 ± 350
Alleröd/Older Dryas		
Older Dryas		
Older Dryas/Bolling		
	GRO 926	11,825 ± 120
	H 77-54	12,300 ± 260
Bolling		
	GRO 927	12,355 ± 170
	GRO 1104	12,300 ± 100
Bolling/Oldest Dryas		
	GRO 928	12,200 ± 100
	GRO 935	12,380 ± 130
	H 88-74	13,250 ± 280
	H 106-89	12,700 ± 320

H—Hiedelberg (Munnich, 1957)

GRO—Groningen (DeVries, et al., 1958)

K—Copenhagen (Anderson, et al., 1953)

W—Washington (Rubin and Suess, 1955 and 1956)

Y—Yale (Barendsen, et al., 1957)

* Not included in average in figure 6.

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